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THE PHYSICAL REVIEW

Published monthly

Two volumes annually

First series. From July 1, 1893 to January 1, 1913, the Review was conducted by Edward L. Nichols, Ernest Merritt and Frederick Bedell, with the financial support of Cornell University. The first four volumes were issued annually; subsequent volumes semi-annually; thirty-five volumes in all.

Second series. On January 1, 1913, the Review was transferred to the American Physical Society as announced on the first page of the new series which was then begun. Since then it has been conducted by a Board of Editors elected by the Society. Semi-annual volumes begin in January and July.

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Annual Subscription, throughout the Postal Union, $7.00 in advance.

Single Copies, $.75.

General Index, 1893-1920, $4.00, in advance.

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Advertisements. Rates will be supplied by the Editor on request. Copy for each number must be received at Corning before the 1st of the preceding month; old copy is used until new copy is received. Send electrotypes direct to the printers, George Banta Publishing Co., Menasha, Wisconsin.

Discount of ten percent is allowed subscription agencies and members of the American Physical Society.

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Correspondence should be addressed to the Physical Review, Corning, N. Y.

Entered at the postoffice at Menasha, Wis., as second class matter.

Acceptance for mailing at special rate of postage provided for in section 1103, Act of October 3, 1917, authorized September 6, 1922

Second Series *July, 1925* *Vol. 26, No. 1*

THE

PHYSICAL REVIEW

THE ISOTOPE EFFECT IN BAND SPECTRA, III. THE SPECTRUM OF COPPER IODIDE AS EXCITED BY ACTIVE NITROGEN

By Robert S. Mulliken[1]

Abstract

Excitation of spectra by active nitrogen.—Band spectra of CuF, CuCl, CuBr, and CuI have been obtained by the action of active nitrogen on the vapors of CuF_2, CuCl and $CuCl_2$, $CuBr_2$, and CuI, using the method of Rayleigh and Fowler, as previously applied by them to CuCl. Certain additional heads are present in the red, probably due to CuO formed as a result of slight oxygen impurity in the active nitrogen, and then excited by the latter. The halide bands are unusually sharp. Probably excited N_2 molecules, in "impacts of the second kind," put halide molecules into the various excited electronic states necessary for the emission of visible band spectra. Many impacts, however, result in dissociation of the halide molecule, as the iodine arc line λ2062 and over 80 lines of the copper arc spectrum were identified. The list of copper lines is exactly the same for CuCl as for CuI. Analogous results have been obtained with PbI_2, HgI_2, and $HgBr_2$. Other reactions of active nitrogen are discussed.

Emission of electronic band spectra by polar molecules.—It is suggested that the absence of electronic band spectra for the hydrogen, silver and alkali halides may be associated with the non-occurrence of higher valence compounds of type $NaCl_2$, and that the emission of any one of the CuX band spectra follows the transfer of a Cu^+ electron in the polar Cu^+X^- molecule from its normal state to one of a group of low lying excited states, whose existence can be correlated with the occurrence of the compounds CuX_2, such easily excited electrons being absent in ions such as Na^+. The above relation may be accounted for by supposing that polar molecules cannot carry electronic energy in excess of their heat of dissociation into atoms. By analogy with the observed absence of electronic band spectra for compounds of the NaCl type, the band spectra of the alkaline earth halides should not be due to compounds MeX_2, since the Me^{++} ion contains no easily excited electron. The real emitter is probably MeX, which must contain a loosely bound valence electron like that in Me^+ or in Na.

Analysis of band spectrum of CuI, and confirmation of vibrational isotope effect.—The CuI bands, excited by active nitrogen, were photographed under moderate dispersion (see Plate I). The wave-lengths of over 260 heads between λ5650 and λ3890 were measured (Tables I-V). No other CuI bands are present between λ1900 and λ7000. Each $Cu^{63}I$ band is found to be accompanied,

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wherever resolution and intensity are sufficient, by a weaker $Cu^{65}I$ band, as expected. The $Cu^{63}I$ bands can all be arranged in *five systems*, the vibrational isotope effect serving as an almost indispensable key to this analysis. One system lies in the green; the other four, with their bands closely intermingled, lie in the blue and violet. Equations are given representing the positions of all the $Cu^{63}I$ heads within experimental error, in terms of the initial and final vibrational quantum numbers and their squares. From these equations, the corresponding theoretical equations for $Cu^{65}I$ are calculated. The observed $Cu^{65}I$ heads fall consistently within experimental error in the calculated positions. Near-equality of the coefficients (of both linear and quadratic terms) concerned with the final state of the molecule, shows that the five systems all correspond to a common final electronic state. This is almost certainly the normal state of the CuI molecule. Analogous relations probably hold for CuCl and CuBr, although the analysis is not yet completed. In all cases the vibration frequency is less and the interatomic distance greater for the excited states than for the normal state. The five excited states of the CuI molecule correspond to electronic energies equivalent to 2.44, 2.68, 2.70, 2.83, and 2.96 volts. *An energy-level diagram* for CuI is given, showing all the electronic and vibrational energy levels, and the observed transitions with their intensities. It is shown that the initial distribution of CuI molecules with respect to vibrational energy is of a thermal type and probably corresponds to the existing low temperature, thus differing markedly from the high-temperature non-thermal distribution characteristic of such compounds as BO and CN as excited by active nitrogen. *Intensity distribution in the CuI bands.* A marked tendency is noted here, as previously in the case of BO, for numerically large values of Δn to be associated with large values of the initial vibrational quantum number n'. This causes the maximum of intensity in band sequences (a sequence contains bands for all of which Δn has the same value) to shift from the first to higher members of the sequence, as one proceeds to bands at increasing distances from the system-origin. Both the above effect and a preference for positive values of Δn are explained in terms of Lenz's theory.

Introduction

THE band spectra of the chloride, bromide, and iodide of copper are highly characteristic, and that of the chloride in particular has been the object of much study.[2,3,4] These spectra all lie in the visible. They consist of numerous groups of bands, every group and every individual band being shaded toward the red. For the appearance of these bands, reference may be made to Eder and Valenta's excellent reproductions.[3] The bands are easily excited by the addition of either cuprous salts (CuCl, CuBr, CuI) or cupric salts ($CuCl_2$, $CuBr_2$) to flames. Cupric salts easily lose their second halogen atom on heating; CuI_2 is so unstable that it cannot be made even at room temperature. Hence, since the cu-

[2] For a summary of the literature, see Kayser and Kayser-Konen, Handbuch der Spektroscopie, vols. V, VII, section on Cu.

[3] J. M. Eder and E. Valenta, Atlas typischer Spektren, Vienna, 1911.

[4] The copper halides are also briefly discussed in H. M. Konen's "Das Leuchten der Gasen und Dämpfe," F. Vieweg und Sohn, Braunschweig, 1913, on pp. 212, 234-5 and 275-6.

pric salts give the same spectra as the corresponding cuprous salts, the spectra have been attributed to the latter.[5] This is confirmed by a quantum theory analysis of the spectra (see below) which shows them to be of the type to be expected for diatomic molecules. The spectrum of copper fluoride (CuF_2) differs from those of the other halides in that it is not readily excited, and in that it consists, so far as is known, only of a single group of bands, which, furthermore, are shaded toward the violet.

Since fairly large isotope effects were to be anticipated in these spectra,[6,7,8] the present study of them was undertaken. The predicted "isotope patterns" have been represented in a diagram on p. 133 of a previous article[8] which will be referred to as (I) in the remainder of the present discussion, and have been confirmed in the actual spectra.[7,8] From the atomic weight, 63.57, the two isotopes of copper which Aston has reported,[9] Cu^{63} and Cu^{65}, should have an abundance ratio of about 5:2. The largest predicted separation between corresponding bands of $Cu^{63}X$ (where X is any halogen) is for CuI, whose spectrum, furthermore, is less complicated than those of CuBr and CuCl, due to the absence of iodine isotopes. Examination of the CuI spectrum was therefore first undertaken. The results of an analysis of the green CuI bands have already been reported briefly.[7] The remainder of the CuI spectrum has now been analyzed, and the complete data and analysis are given below, together with preliminary and general results on CuCl and CuBr. The latter will be treated more in detail in a later paper.

Use of Active Nitrogen in Excitation of Copper Halide Spectra

In their classic work on active nitrogen, Rayleigh and Fowler showed[10] that the CuCl band spectrum can be excited by the introduction of CuCl vapor into the nitrogen afterglow. They reported that the CuCl bands are better visible than in the flame, the usual continuous background[11] in the green being absent. They also found more bands than usual at the ultraviolet end, and further noted that the copper

[5] R. Derichsweiler, Dissertation Bonn, 1906; Zeits. wiss. Phot. **4**, 401-17 (1906).

[6] R. S. Mulliken, Nature, April 5, 1924.

[7] R. S. Mulliken, abstract of paper given at meeting of Amer. Phys. Soc., Phys. Rev. **23**, 767 (1924).

[8] R. S. Mulliken, Phys. Rev. **25**, 119 (Feb., 1925): The Isotope Effect in Band Spectra, Part I.

[9] F. W. Aston, Isotopes, 2nd ed., 1924. Edw. Arnold & Co., London.

[10] R. J. Strutt, Proc. Roy. Soc. **85A**, 219 (1911);
R. J. Strutt and A. Fowler, Proc. Roy. Soc. **86A**, 105 (1911).

[11] This is observed in the flame spectra of all copper salts. Apparently it is not really continuous but consists (see ref. 3) of numerous closely-spaced bands (oxide bands?).

arc spectrum was developed, more lines being present than in the flame.

On account of the sharpness and clearness of the heads, and also because of interesting possibilities in regard to the mechanism of excitation, the writer has used active nitrogen as a means of exciting the spectra of all the copper halides. It was found that the bromide ($CuBr_2$ was used) and especially the iodide, (CuI) are less readily excited than the chloride (either CuCl or $CuCl_2$), more intense heating and longer exposures being required. Also, the iodide band spectrum is largely masked by the presence of even a small amount of chloride impurity. The intensity of the copper line spectrum, relative to that of the band spectrum, appears to increase markedly in going from chloride to iodide. These differences would seem to be correlated with decreasing stability of the molecules in the order chloride-bromide-iodide. The excitation of the fluoride spectrum, by heating CuF_2 in active nitrogen, was found even more difficult than that of the iodide spectrum, perhaps on account of the involatility of CuF_2; some weak exposures were, however, obtained.

Oxide bands. With all three halides, a set of bands, of variable intensity, occurs in the red. These proved, by approximate determination of their wave-lengths and comparison with Eder and Valenta's excellent reproductions,[12] to be the red bands which are ascribed by Eder and Valenta to copper oxide (CuO), and which occur in the flame spectra of all copper salts. The heads of the bands appear for the most part in pairs, all the heads being shaded toward the red. According to the literature, the members of a pair are ordinarily about equally intense, but in the present experiments, the shorter wave-length component was relatively weak. The following list covers the observed heads, the intensities being given in parentheses, for an unusually intense exposure. The wave-lengths were not carefully measured, but Hertenstein's values[13] are given approximately, except for three apparently new heads at the red end for which the (only roughly approximately) wave-lengths are italicized: λ6046 (1), 6060 (7); 6148 (2), 6163 (8); 6283 (00?), 6296 (2); 6381 (0), 6403 (1), *6435* (3); *6490* (1), *6530* (1), 6547 (2). Only the stronger heads (int. 2 or

[12] Eder and Valenta.[3] Plates V, 2-3, XXI, 9, and XXV, 8, show these bands especially well. In plate XXI, 9, the stronger heads are shown resolved into what is probably a succession of heads, so that each "head" as used above probably means the first head of a compact group. Kayser and Konen[2] consider it rather doubtful whether these and other bands toward shorter wave-lengths are due to the oxide or the metal. Some of the copper bands of large spacing, as well as other supposed metal bands, have recently been shown (see ref. 6) to be due to a hydride. The red bands are not of this type. It is of course still possible that they are due to Cu_2.

[13] H. Hertenstein, Zeits. wiss. Phot. **11**, 69 and 119 (1912).

more) were definitely observed to be shaded toward the red. It may be noted that only the heads from λ6046 to 6296 are found in the Bunsen flame, according to Eder and Valenta, while the oxy-gas flame is needed for the following pair. The occurrence of the bands here is presumably due to the excitation of oxide molecules by active nitrogen. A detailed investigation did not seem worth while, but there was evidence that the bands are favored by a small leakage of air into the halide vapor, or the presence of a little oxygen in the nitrogen used. A dark brown or black deposit, presumably copper oxide, formed in small amounts on the walls of the afterglow tube, was formed more rapidly when air was admitted. This product, separated from copper halide by dissolving the latter in sodium thiosulphate solution, was at first suspected of being a nitride. On heating it with NaOH solution, a strong odor of ammonia was in fact obtained in one case when CuBr had been used (in this case the NaOH was added directly to the thiosulphate solution containing the solid in suspension). Since, however, later tests with Nessler's reagent failed to give any indication of ammonia with the product obtained from CuI, and only a slight test with the CuCl product, the formation of nitride in appreciable amounts must be considered very doubtful.—There is no evidence in the present work of a nitride band spectrum.

Experimental Methods and Wave-Length Data

In producing the active nitrogen, the method used was essentially that of Lord Rayleigh.[14] Commercial nitrogen (99.7 per cent pure according to the manufacturers) contained in a cylinder under pressure was passed through successive tubes containing (a) fragments of yellow phosphorus (b) calcium chloride, (c) soda-lime, (d) phosphorus pentoxide.

The product was usually very nearly free from oxygen—the β and γ bands of active nitrogen, which are due to the presence of oxygen, being very weak—and sometimes contained excess phosphorus vapor. Any considerable amount either of oxygen or of phosphorus vapor caused a marked decrease in the intensity of the copper halide bands. In experiments with CuCl where excess phosphorus vapor was present, it was found that the CuCl spectrum was restored to its original brilliancy by the admission of a small amount of air, sufficient to destroy the phosphorus. The effect was the same whether this was added before or after the activation of the nitrogen, and the amount required had no visible effect on the color or intensity of the afterglow itself.[15]

[14] R. J. Strutt, Proc. Roy. Soc. **85A**, 219 (1911).

[15] The effect of adding oxygen here was evidently of an entirely different nature from that in the case of BO (R. S. Mulliken, Nature, Sept. 6, 1924), where no excess of phosphorus was present.

Description of Plate I

Plate I shows most of the CuI bands; *top*, A bands; *middle*, B, C, most of D, and part of E bands; *bottom*, one D band and part of E bands (there are probably a few more, not shown, toward the ultraviolet). Each $Cu^{63}I$ head is marked with a vertical line. Each horizontal line serves to connect the members of a band-sequence, i.e. a set of bands having a common value of $(n''-n')$, n'' and n' being the final and initial vibrational quantum numbers. For each system, the first head $(n', n'') = (0,0)$ of the (0) sequence is marked by a *very* heavy vertical line, accompanied by the letter (A, B, etc.) which has been assigned to the system. With this as an origin, the numbering of the other sequences and of the individual bands can be found very readily from the reproduction. Thus, in the A system, the (0) sequence, from left to right, contains the bands (0,0), (1,1), (2,2), (3,3), . . . The next sequence (+1) on the right, contains the bands (0,1), (1,2), (2,3), (3,4), (4,5), . . . On the left of the origin is the (−1) sequence, with bands (1,0), (2,1), (3,2), (4,3), (5,4), . . . ; with the (5,4) head, this sequence slightly overlaps the (0) sequence. It will be noted that on each side of the origin the spacing of the first heads of successive sequences is approximately constant, but that it differs markedly for the positive and negative sequences. This is because these first heads are (0,0), (1,0), (2,0), (3,0), . . . for the negative, and (0,1), (0,2), (0,3), . . . for the positive sequences. For the former the spacing is determined by the *initial*, for the latter by the *final*, vibration frequency of the molecule. To avoid confusion, alternate sequences have been marked in the A bands by verticals of different height; while in the B, C, D, and E bands, which are badly mixed together in the middle of the spectrum, a vertical of characteristic height (diminishing in the order named) is used for each.

The A bands in particular show a typical intensity distribution. As can be seen in the reproduction, the sequences near the origin are the most intense, with some preference for the positive sequences. In the low-numbered sequences, the first head is the most intense, but the intensity maximum shifts to the second head with the sequences ± 3, and to higher-numbered heads for the higher sequences.

For each $Cu^{63}I$ head, there is a corresponding weaker $Cu^{65}I$ head *nearer the origin* in each case. These begin to be resolved at about the sequences ± 2. In the reproduction, resolution is apparent in the A system at +3, in the other systems (except B, which is too faint) at +2. In the negative sequences, the $Cu^{65}I$ heads are not visible, except rather vaguely in the A sequences −3 and −4. This is due partly to low intensity, partly to concealment by the shading of corresponding $Cu^{63}I$ heads. Examination of the manner in which, in the positive sequences, the separation between the heads of the two isotopes converges toward zero as the origin is approached, will show the value of the isotope effect as a means of locating the latter. (Casual inspection of the reproduction would probably lead to a false assignment, due to the different intensities of the heads of the two isotopes; the (+1) sequence would probably be called (0). Careful inspection of the original negative, however, and especially measurement gives the correct assignment without difficulty.)

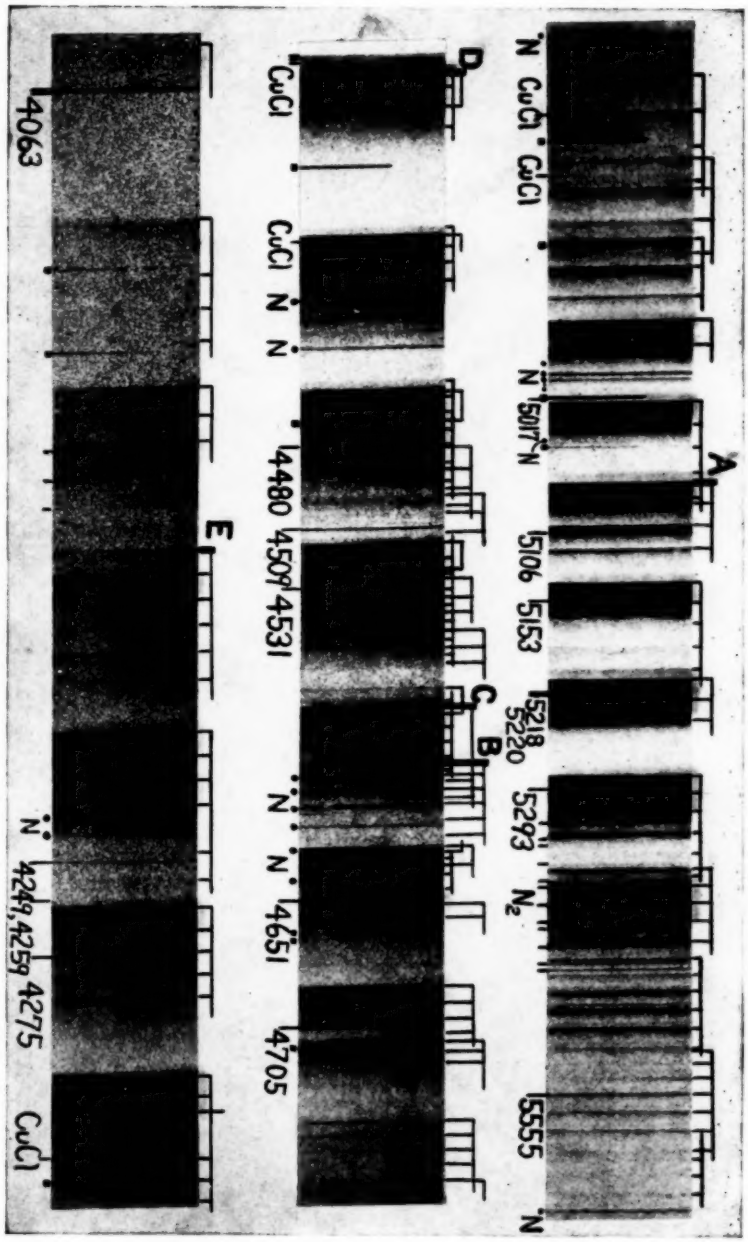

Plate I. Spectrograms showing most of the CuI bands.

The discharge tube for activating the nitrogen, and the attached afterglow tube, were of Pyrex glass of about 8 mm internal diameter. The arrangement is shown in Fig. 1. The discharge was maintained between two tungsten electrodes which were about 10 cm apart. A type E Clapp-Eastham transformer was used at maximum amperage on a 110 volt circuit, with a spark-gap and two large Leyden jars in parallel in the secondary circuit. The activated nitrogen was pumped rapidly out, through a black-painted light trap *T*, into the afterglow tube. The latter was attached at right angles to the discharge tube. The copper salt was contained in a small bulb *B* connected to the afterglow tube at a point just below the point of entrance of the active nitrogen. The bulb was heated by a Bunsen flame just short of its softening point. The quartz

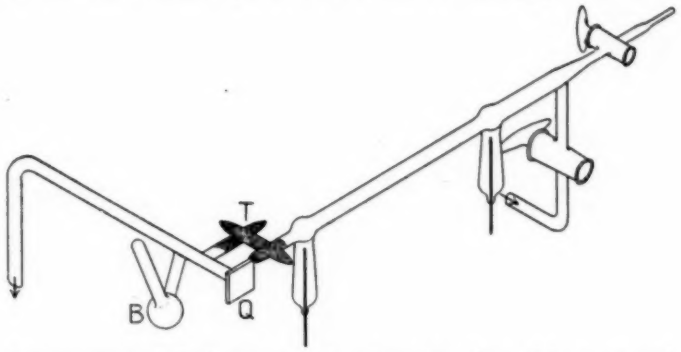

Fig. 1. Arrangement of discharge and afterglow tube for exciting spectra by means of active nitrogen.

window *Q*, fastened with DeKhotinsky cement, was kept cool by means of a ring of wet filter paper on the adjacent section of the afterglow tube. The discharge tube terminal nearer the afterglow tube was earthed, to prevent stray discharge through the latter. In early experiments, where this precaution was not taken, nitrogen lines were present in the spectrum; they were absent from the later photographs, although nothing else was changed. A nitrogen flow rate of 20-60 liters (at 1 atmosphere pressure) per hour was used, with a pressure of about 15-40 mm in the afterglow tube.

The spectra were photographed with a Hilger glass constant-deviation prism spectrograph. The dispersion ranged from about 12 A/mm at λ4000 to 36 A/mm at λ5000 and 72 A/mm at λ6000. Panchromatic, special green-sensitive, and contrast plates were used for best results with the red, green, and blue to violet regions, respectively. The ultraviolet was examined with quartz spectrographs.

As wave-length standards for the bands, the interspersed Cu lines were used, supplemented by helium lines (plus Hβ, Hγ, and Hα) from a super-

posed comparison spectrum, and in the yellow-green, where Cu lines were scarce, by certain N_2 band-heads of the first positive group (α bands of the afterglow); the latter are very sharp and appear to have been measured accurately to 0.01A. In one photograph N lines resulting from stray discharge (see above) were also available.

In the case of CuI, the exposure used for measurement was one of about three hours duration on a special green-sensitive plate. Enlargements from this are shown in Plate I. The type of plate used is fine-grained, and so, with good focus and a narrow slit, permitted unusually good resolution for the size of the instrument. Practically every distinct head on the plate, including very weak ones, was carefully measured. The results are given in Tables I-V. It can be stated definitely that there are no additional bands of appreciable intensity, at least in the region λ1900-7000. The precision of the measurements can be gauged by the magnitude of the values in the Obs.-Calc. (O-C) columns. A slight constant error is

TABLE I

A bands

Note for Tables I-V: The vibrational quantum numbers are given under n' and n''. The "calculated" wave-numbers used for computing the values under "O-C" (observed minus calculated) for $Cu^{63}I$ and in obtaining the calculated isotopic displacements, were obtained from the equations of Table 6. Isotopic displacements, i.e. $\nu(Cu^{65}I) - \nu(Cu^{63}I)$, are given in wave-number units. Wave-numbers in brackets are calculated values, inserted where measurements were not obtained. Nitrogen lines (due to stray discharge, see above), of which a small number were present, and which in some cases (marked "also N line") were superposed on CuI heads, could be picked out by the fact that they extended beyond the CuI heads at the edges of the exposure.

		Cu^{63} I heads				Cu^{65}I heads			Isotopic displacement	
n'	n''	Int.	λ(I.A.)	Wave-no.	O–C	Int.	λ(I.A.)	Wave-no.	Obs.	Calc.
8	3	0	4886.0	20461	−10	0–*	4887.6	20454	−7	−6.7
4	0	0	72.77	516.5	−2	0*	74.69	508.4	−8.1	−8.0
5	1	0+	89.57	446.0	0	0+*	91.15	439.4	−6.6	−7.1
6	2	0	4917.93	369.5	−1	0*	4909.40	363.4	−6.1	−6.2
7	3	00	28.4	285	−7	00*	29.6	280	−5	−5.2
3	0	1	19.09	323.3	1	1*	20.86	316.0	−7.3	−6.1
4	1	1	35.59	255.4	1	1–*	36.73	250.7	−4.7	−5.4
5	2	0	53.16	183.5	0	0*	54.19	179.3	−4.2	−4.5
6	3	00		[109.3]						
7	4	00		[031.9]						
2	0	3	68.33	121.9	0		69.24	118.2	−3.7	−4.2
3	1	2	83.88	059.1	0		84.85	055.2	−3.9	−3.5
4	2	0		[19992.2]						
5	3	00		[920.4]						

* The high apparent intensities of the $Cu^{65}I$ heads in this region are due to their superposition on the shading from corresponding $Cu^{63}I$ heads.

TABLE I—continued

n'	n''	$Cu^{63}I$ heads Int.	λ(I.A.)	Wave-no.	O−C	$Cu^{65}I$ heads Int.	λ(I.A.)	Wave-no.	Isotopic displacement Obs.	Calc.
1	0	5	5019.74	915.8	−1					−2.1
2	1	1	34.61	857.0	−1					−1.6
3	2	000		[796.3]						−0.9
4	3	0	66.65	731.4	0					−0.2
5	4	0+	84.52	662.1	−1					0.6
6	5	00		[591.5]						
0	0	7	72.83	707.4	0					0.0
1	1	0+	87.16	651.9	−1					0.5
2	2	1	5101.92	595.0	−1					1.0
3	3	1	17.31	536.1	1					1.6
4	4	000		[471.5]						
0	1	5	41.12	445.6	2					
1	2	1	55.84	390.1	−1					
2	3	00−	70.75	334.2	−1	000		[19338.7]		3.6
3	4	0	86.80	274.4	−1	00	5185.95	277.5	3.1	4.2
4	5	0	5202.74	215.3	2	00	5201.18	221.1	5.8	4.9
0	2	5	12.18	180.5	−1	2	10.71	185.9	5.4	5.2
1	3	3	26.08	129.5	0	1	24.28	136.1	6.6	5.7
2	4	1	41.03	074.9	0	0	39.25	081.4	6.5	6.1
0	3	2	83.80	18920.5	0	0	81.80	18927.7	7.2	7.8
1	4	4	97.55	871.4	1	1	95.17	879.9	8.5	8.2
2	5	3	5312.42	818.6	2	1	5310.05	827.0	8.4	8.7
3	6	1	28.53	761.7	1	0	26.09	770.3	8.6	9.2
4	7	00	45.8	701	−1	000	43.8	708	7	9.8
5	8	0	64.09	637.3	−1	0	61.3	647	10	10.5
0	4	1	57.42	660.5	0	0	54.27	671.5	11.0	10.3
1	5	3	71.47	611.7	0	1	68.16	623.2	11.5	10.7
2	6	4	86.50	559.8	0	2	83.22	571.1	11.3	11.1
3	7	3†	5402.18	506.1	1	1	98.74	517.7	11.6	11.6
4	8	1−	18.94	448.7	1	0−	5415.71	459.7	11.0	12.2
0	5	0	33.48	399.3	−3	00	28.03	417.8	18.5	12.9
1	6	0+	46.60	355.0	0	1†	42.41	369.1	(14.1)	13.2
2	7	1	61.30	305.6	1	0	57.45	318.5	12.9	13.6
3	8	2	77.09	252.8	1	1	73.04	266.3	13.5	14.1
4	9	1	94.07	196.4	2	0	89.88	210.3	13.9	14.6
5	10	0	5512.79	134.6	−1	00	5507.72	151.3	16.7	15.3
0	6			[145.4]						15.3
1	7	00	24.34	096.7	−3	000	19.1	114	17	15.6
2	8	0	38.88	049.2	−2	00	34.07	064.9	15.7	16.0
3	9	1−	54.02	000.0	1	0	48.16	019.0	19.0	16.5
4	10	0+	71.04	17945.0	1	0−	65.21	17963.8	18.8	17.0
5	11	0	88.76	888.1	3	00	83.29	905.6	17.5	17.6
6	12	00	5608.9	824	0	00	5603.8	840	16	18.3
2	9	000	17.3	797	−1					18.4
3	10	00	32.5	749	1	000	26.8	767	18	18.9
4	11	00	49.7	695	1	000	43.1	716	21	19.4

† Also N_1 head.

Note: Average value of "observed" minus "calculated" isotopic displacement, excluding from the average only (0,5), (1,6), and bands where the $Cu^{65}I$ head has an intensity less than 00, is +0.05.

TABLE II

B bands

Note: because of the low intensity or absence of bands for which an appreciable separation of the heads of the two isotopes would be expected, no measurements could be made on $Cu^{65}I$ heads. Indications of the (0,2) head of $Cu^{65}I$ were seen, however.

n'	n''	$Cu^{63}I$ heads Int.	λ(I.A.)	Wave-no.	O−C	Remarks
2	0	0−	4498.26	22224.6	0	
3	1	00	4504.79	192.4	0	
4	2	00	11.19	160.9	2	Also 1, 8 E ($Cu^{65}I$)
1	0	1−	46.77	21987.5	−1	
2	1	0	52.63	959.2	−1	
3	2	00	58.11	932.8	3	
4	3			[897.9]		
0	0	1d	96.95	747.5	−1	Also (weak) 3,3C
1	1	1	4601.58	725.6	2	Also (strong) N line
2	2	1	07.07	699.7	2	Also (strong) N line
3	3	00	13.09	671.4	2	
4	4	00	19.95	639.2	0	
5	5	00	26.60	608.1	0	
6	6			[574.3]		
0	1	0+	4653.50	21483.2	−1	
1	2	0−	58.62	459.6	−2	Also 4, 5C?
2	3			[437.1]		A group of heads (see footnote) present here may include both B and C heads; but the data do not agree well with either.
3	4			[411.0]		
4	5			[383.1]		
5	6			[353.4]		
0	2	0−	4711.34	219.5	−2	
1	3	00	15.00	203.0	2	Also 4,6 C?
2	4	00	19.85	181.2	3	
3	5	00d	23.69	164.0	9	Fused with 5,7 C?
4	6			[128.7]		Possibly present but confused by C heads.
5	7			[101.0]		

Note: wave-numbers of unidentified heads, with intensities: 21342.1(00); 21357.5 (00−); 21370.3 (00); 21386.5 (00); 21402.9 (0−); 21417.7 (00); 21431.2 (0−); 21445.2 (00); 21473.7 (0); 21548.2 (00); 21581.1 (00?); 21657.3 (00); 21691.1 (00); 21710.8 (00); 21739.0(00?); 21823.0 (00); 21905.7 (00); 22178.0 (00); 22192.4 (00); 22418.4 (00+); 22431.9 (00); 22771.0 (00); 22802.4 (00); 22833.3 (00); 22866.8 (00).

TABLE III

C bands

n'	n''	$Cu^{63}I$ heads Int.	λ(I.A.)	Wave-no.	O–C	$Cu^{65}I$ heads Int.	λ(I.A.)	Wave-no.	Isotopic displacement Obs.	Calc.
3	0	weak or absent,		[22534.9]						
4	1	masked by CuCl		[497.7]						
2	0	00	4482.03	305.1[1]	−3					
3	1	00?	89.81	266.4	−5					
4	2	00–	96.88	231.4	−4					
5	3	00	4502.41	204.1	4					
6	4			[165.3][2]						
1	0	2–	27.92	079.0	−1					
2	1	0–	35.11	044.0	−1					
3	2	00	41.91	011.0	1					
0	0	2–	75.15	21851.1	0					
1	1			[816.9]						
2	2	masked by 5,13 E		[782.8]						
3	3	masked by 0,0 B		[749.2]						
4	4	00	4603.31	717.4	1					
5	5	00	10.64	682.9	0					
0	1	3?	30.63	589.3	1					
1	2	0	38.03	554.9	0					
2	3	..	....	[522.2]						
3	4	masked by Cu		[489.9]						
4	5	0–	58.62	459.6[3]	2					
5	6			[426.4][4]						
6	7			[395.3][4]						
7	8			[364.6][4]						
8	9			[334.3][4]						
0	2	1+	87.80	326.0	0	0	4686.84	21330.4	4.4	5.4
1	3	1–	93.97	295.3	1	0–	93.35	300.8	5.5	5.7
2	4	0–	4701.72	262.9	0	00	4700.21	269.7	6.8	6.0
3	5	00	08.72	231.3	−1					
4	6	00	14.99	203.0[5]	2					
5	7	00d	23.69	164.0[6]	−7					
6	8	00	29.54	137.8[7]	−3					
7	9	00	35.59	110.8[7]	−1					
0	3	00	45.96	064.7	−1	00	43.59	075.2	10.5	8.0
1	4	0+	52.64	035.1	0	00	50.90	042.8	7.7	8.3
2	5	00+	59.35	005.4	0	00	57.47	013.7	8.3	8.6
3	6	00–	66.14	20975.5	0	00–	64.37	20983.3	7.8	8.8
4	7	00	72.81	946.2[8]	0					
5	8			[917.0][9]						
6	9			[888.5]						
0	4	00?	....	[806.4]						
1	5	00?	....	[777.1]						
2	6	00?	....	[748.3]						

[1] Also 6,12 ($Cu^{65}I$).
[2] Confused by E and B heads.
[3] Also 1,2 B.
[4] See remark in Table II on heads in this region.
[5] Also 1,3 B.
[6] Fused with 3,5 B?
[7] Confused by B heads, see Table II.
[8] Also 0,3 B.
[9] Confused by B.

TABLE IV

D bands

n'	n''	$Cu^{63}I$ heads Int.	λ(I.A.)	Wave-no.	O−C	$Cu^{65}I$ heads Int.	λ(I.A.)	Wave-no.	Isotopic displacement Obs.	Calc.
2	0	?0−	4281.97	23347.2[1]	..					
1	0	1	4320.01	141.6	0					
0	0	2+	59.95	22929.6	0					
1	1	1+	69.93	877.3[2]	−1					
0	1	3	4410.76	666.0	0					
0	2	2	62.22	404.1	0	0+	4461.08	22409.8	5.7	5.4
1	3	1	71.64	356.9[3]	2					
0	3	1	4514.76	143.4[4]	0	0	4513.31	150.5	7.1	8.0
1	4	0	24.69	094.8	0	0+	22.46[5]	105.7	10.9	8.4
0	4	0-d	68.50	21882.9	0	0−	66.31	21893.4	10.5	10.6
1	5	0d	78.15	836.8[6]	0		masked by 0,0 C			
1	6	00	4632.39	581.1	2					

[1] Doubtful, in shading of 3,5E.
[2] Also 2,6 E.
[3] Also (weak) 3,9 E ($Cu^{65}I$).
[4] Also (weak)1,8 E .
[5] Also 3,10 E ($Cu^{65}I$).
[6] Also 3,11 E.

TABLE V

E bands[1]

n'	n''	$Cu^{63}I$ heads Int.	λ(I.A.)	Wave-no.	O−C	$Cu^{65}I$ heads Int.	λ(I.A.)	Wave-no.	Isotopic displacement[2] Obs.	Calc.
3	0	0	4054.17	24659.0	0					
4	1	..	....	[617.4]	..					
2	0	1	91.32	435.1	0					
3	1	0	....	[395.8]						
4	2	0	4105.02	353.6	−2					
5	3	0	12.34	310.2	−5					
6	4	00	18.51	273.8	0					

[1] Besides the heads recorded in the table, some additional weak heads, mostly further toward the ultraviolet, were found in photographs with the quartz spectrograph. These are shaded toward the red, like the other CuI bands. Several attempts were made to obtain these bands in sufficient intensity for good measurements, but this finally appeared to be not worth while. The data below were obtained with a weak exposure and wide slit. The presence of CN and CuCl bands as impurities also increased the difficulties; NO and I_2 bands were not present in this region. They suffice, however, in spite of poor agreement with calculated values, to establish without much doubt that the observed bands are a (not unexpected) continuation of the E bands, and not an independent system. The intensities were for the most part too low for identification of $Cu^{65}I$ heads. The measured values are (with calculated values in parentheses): 24526, (int. 00) (6,3 E = 24533); 24656, (0) (3,0 E = 24659); 24875, (00) (4,0 E = 24881); 24983, (00); 25045, (00) (6,1 E = 25055); 25079, (00) (5,0 E, $Cu^{65}I$, = 25089); 25090, (00) (5,0 E = 25100); 25235, (00), superposed on CuCl head (8,2 E = 25223); 25265, CuCl head (7,1 E = 25271); 25311, (00d) (25318 = 6,0 E); 25378, (000d); 25493, (00d) (8,1 E = 25485); 25533, (000d) (7,0 E = 25534); 25647, (000) (9,1 E = 25697); and perhaps a few additional weaker heads.

[2] Average value of "observed" minus "calculated" isotopic displacement, excluding heads marked * or ?, or of intensity less than 0, is −0.4.

TABLE V—continued

n'	n''	$Cu^{63}I$ heads Int.	λ(I.A.)	Wave-no.	O-C	$Cu^{65}I$ heads Int.	λ(I.A.)	Wave-no.	Isotopic displacement Obs.	Calc.
1	0	1−	29.38	209.9	0	*0?	4130.32	24204.4[3]	−5.5	−2.3
2	1	0	35.82	172.2	0	*0−?	36.49	168.3[3]	−3.9	−2.0
3	2	0	42.22	134.9	1					
0	0	0	68.52	23982.6	0					
1	1	2	74.60	947.6	1					
2	2	1−	80.85	910.9	0					
3	3	00	87.55	873.6	0					
4	4	0+	94.12	836.2	0					
5	5	00	4200.98	797.3	−1					
0	1	2	14.64	720.2	1	0?	.....	.....	.....	2.7
1	2	0	21.03	684.2	−1					
2	3	2−	27.00	650.8	1	0−	4226.39	23654.2	3.4	3.5
3	4	0	33.75	613.1	−1					
4	5	000	.....	[578.3]						
5	6	00	47.01	539.4	−2					
6	7	00	53.28	504.7	0					
0	2	3	61.74	458.1	0	1	60.72	463.6	5.5	5.4
1	3	0−	68.14	422.8	−2	...	.....	[428.5]	.....	5.7
2	4	00	74.11	390.1	−1	?00	72.83	397.1	7.0	6.0
3	5	1−	80.06	357.5	1	0−	79.07	363.4	5.9	6.4
4	6	1−	86.50	322.5	1	00	.....	[329.3]	.....	6.8
5	7	000	.....	[286.5]						
0	3	2+	4309.62	197.4	0	1−	4308.17	205.2	7.8	8.0
1	4	1	15.42	166.2	1	0	14.06	173.5	7.3	8.3
2	5	.....	masked	[133.2]		*	masked	[141.8][4]	.....	8.6
3	6	000	.....	[100.3]				[109.2]	.....	8.9
4	7	0*	masked	[066.8][5]		00	32.30	076.0	[9.2]	9.3
5	8	0−	40.45	032.6	0	00	39.02	040.2	7.6	9.6
6	9	00	46.80	22999.0	1					
0	4	1*	58.34	938.1[6]	0	0*	56.19	22949.4[6]	(11.3)	10.7
1	5	2−	64.05	908.1	0	0+	62.12	918.2	10.1	10.9
2	6	1+*	69.93	877.3[7]	1	0−	68.00	887.4	10.1	11.2
3	7	0−	76.11	844.9	0	00	74.11	855.4	10.5	11.4
4	8	000	82.27	812.8	0	000	79.95	824.9	12.1	11.7
5	9	00−	88.55	780.2	0	000	86.60	790.3	10.1	12.0
6	10	000	94.86	747.5	0	000	92.77	758.3	10.8	12.4
7	11	000−		[713.2]						
0	5	0+	4408.07	679.3	−1	0−	4405.53	692.4	13.1	13.2
1	6	1−	13.75	650.1	−1	*	masked	[663.6][8]	....	13.5
2	7	1*	19.08	622.8[9]	1	0+	16.62	635.4	12.6	13.7
3	8	1−	25.07	592.2	1	0−	22.50	605.3	13.1	14.0
4	9	0*	31.25	560.7[10]	0	00		[575.0]		14.3

[3] Intensity doubtful.
[4] Masked by 1,0 D.
[5] Masked by CuCl.
[6] Also CuCl?
[7] Also 1,1 D.
[8] Masked by 0,1 D.
[9] Also 1,2 D.
[10] Also N λ4431.

TABLE V—continued

n'	n''	$Cu^{63}I$ heads Int.	λ(I.A.)	Wave-no.	O—C	$Cu^{65}I$ heads Int.	λ(I.A.)	Wave-no.	Isotopic displacement Obs.	Calc.
0	6	0	58.40	423.3	−1					
1	7	1	63.60	397.2	1					
2	8	1+	69.24	368.9	1	1d	65.93	385.5	16.6	16.2
3	9	1+	75.05	339.9	1	1*+	71.64	356.9[11]	17.0	16.4
4	10	1−	masked	[309.6][12]		0–d	78.01	325.1	.....	16.7
5	11	0–d	86.89	280.9	1	0−	84.42	293.2	12.3	16.9
6	12	00d	93.69	247.2	−2	00	89.81	266.4	19.2	17.2
0	7	.....	masked	[168.9][12]		00	4506.19	185.5	.....	18.4
1	8	1*+	4514.76[13]	143.4	1	00*	11.19	160.9[13]	[17.5]	18.5
2	9	0+	20.62	114.7	−1	0+	16.94	132.7	18.0	18.7
3	10	0+	26.28	087.0	−1	0*+	22.46	105.7[14]	18.7	18.9
4	11	00	31.88	059.7	0	...	masked[15]	[078.6]		19.1
5	12	0	37.65	031.7	1	0−	33.36	052.5	20.8	19.3
6	13	0d	43.71	002.3	0	00	39.07	024.8	22.5	19.5
7	14	00−	49.73	21973.2	1					
8	15	00	55.93	943.3	2					
2	10	00d	72.80	862.3	−2					21.2
3	11	0d*	78.15	836.8[16]	−1	masked by 2,10 of $Cu^{63}I$				21.3
4	12	0d	83.46	811.5	0	masked by 3,11 of $Cu^{63}I$				21.5
5	13	0d*	88.95	785.4[17]	1	masked by 4,12 of $Cu^{63}I$				21.7
6	14	00d	94.69	758.2	2					21.9
7	15	00	4600.23	732.0	4					
3	12	*	masked	[589.3][18]	−1					
4	13	00	35.80	565.2	1					
5	14	00	41.50	538.7	0					
6	15	0–d	49.24	508.9	−3					

[11] Also 1, 3 D.
[12] Masked by Cu.
[13] For 4514, also (strong) 0,3 D; for 4511, also 4,2 B.
[14] Also (strong) 1,4 D.
[15] Masked by 1,0 C.
[16] Also 1,5 D.
[17] Also 2,2 C.
[18] Masked by 0,1 C.

likely, due to the uncertainty as to the proper mode of setting on heads which are shaded off toward one side. The following measured values for a few of the strongest CuCl heads, present as impurities among the CuI heads, may be compared with presumably much more accurate values as determined by Kien[16] under high dispersion:

Present results: 4333.37, 4353.93, 4412.16;

Kien, 4333.254, 4353.892; 4412.14.

Detailed data on the CuBr and CuCl bands will be reserved for a later paper.

ANALYSIS OF CuI BANDS

As will be seen from the tables, all the CuI bands, with a few very weak and rather doubtful exceptions, can be arranged in five band-

[16] P. Kien, Diss. Bonn. 1908; Zeits. wiss. Phot. **6**, 337 (1908).

systems, i.e., five complex groups of bands, each associated with a particular electronic transition in the CuI molecule, accompanied by a variety of vibrational transitions indicated by the values of the initial and final vibrational quantum numbers n' and n''. For simplicity, and in the absence of direct evidence from the present analysis, integral vibrational quantum numbers are here used in accordance with the usual practice, although the isotope effect in the BO spectrum[17] indicates that half-integral values may be needed. The assignment of vibrational quantum numbers is such as to satisfy the criteria used by Heurlinger and Kratzer, as well as the isotope effect criterion (I, p. 136).[8] The isotope effect, as previously emphasized,[7,8] was invaluable in locating the origins of the band-systems, giving, in fact, the first clue to the analysis of the very complex spectrum. In examining the arrangements of the bands in the tables, comparison with the reproduced spectrum (Plate I, and accompanying explanation) will be useful.

In Table VI are given, for each CuI system, equations in terms of the parameters n' and n'' capable of representing within experimental error the positions of all the measured heads. The possibility that cubic

TABLE VI

Equations representing CuI heads

Note: the equations, except those for $Cu^{65}I$, were obtained by plotting the appropriate first differences; the $Cu^{65}I$ coefficients were calculated according to theory from those of the corresponding $Cu^{63}I$ equations.

A bands

$Cu^{63}I$: $\nu = 19,707.65 + 211.91n' - 2.283n'^2 - 264.63n'' + 0.713n''^2$
$[Cu^{65}I$: $\nu = 19,707.7 + 209.72n' - 2.236n'^2 - 261.89n'' + 0.698n''^2]$

B bands

$Cu^{63}I$: $\nu = 21,748.3 + 241.8n' - 1.88n'^2 - 265.4n'' + 1.0n''^2$

C bands

$Cu^{63}I$: $\nu = 21,851.41 + 229.17n' - 0.447n'^2 - 263.86n'' + 0.653n''^2$
$[Cu^{65}I$: $\nu = 21,851.4 + 226.80n' - 0.438n'^2 - 261.14n'' + 0.640n''^2]$

D bands

$Cu^{63}I$: $\nu = 22,929.66 + F(n') - 264.2n'' + 0.64n''^2$
$[Cu^{65}I$: $\nu = 22,929.7 + 0.99F(n') - 261.5n'' + 0.63n''^2]$
Note: $F(n') = 212.1$ for $n' = 1$.

E bands

$Cu^{63}I$: $\nu = 23,982.71 + 228.28n' - 0.954n'^2 - 263.81n'' + 0.671n''^2$
$[Cu^{65}I$: $\nu = 23,982.7 + 225.92n' - 0.934n'^2 - 261.09n'' + 0.657n''^2]$

terms in n' (and n'') should be used has been disregarded, since the data are not precise enough to yield significant values of the coefficients of such terms. The coefficients, and especially the constants, of Table VI are, of course, somewhat influenced (cf I, pp. 131-2) by the fact that the

[17] R. S. Mulliken, Phys. Rev. **25**,259 (March, 1925).

data refer to heads, instead of to origins (I, p. 123) or null-lines. This fact does not, however, obscure certain important major relations among the various bands. In fact, the present type of analysis, in which the arrangement of bands in systems is determined without regard to band-structure, seems to the writer a desirable preliminary, in complex cases like those of the copper halides, to a more detailed analysis of individual bands under higher dispersion.[18]

Considering for the present only the $Cu^{63}I$ heads, one of the most striking facts revealed in Table VI is the near-identity of all coefficients of n'' and n''^2 for all five systems.[19] The agreement is so close as to make it extremely probable that the final electronic state (and associated vibrational states) are the same for all five systems. The differences in the coefficients and—what is more important—in the final state vibrational energy terms[19] for the different systems are small enough to be accounted for by the errors involved in their determination together with the fact that the coefficients and energy terms contain small contributions (I, p. 132) which differ from one system to another, due to the fact that the data refer to heads. The agreement is least good in the B system, where the reliable data are fewest. Granting that all five CuI band systems have the same final electronic state, it would seem that there is something peculiarly stable or normal about this state. There can, in fact, in view of the ready excitation of these bands and no others in the comparatively low temperature of the Bunsen flame,[3] taken together with the fact that they involve

[18] On p. 212 of Konen's book[4] the copper halide spectra are classed as "Pseudokantenspektra" because the band heads become less and less conspicuous with increasing dispersion and in many cases finally disappear. On account of this behavior, Konen apparently considers it very doubtful whether the heads are genuine. The present analysis shows that the arrangement of the heads is completely in agreement with that found in other typical cases where no such question has been raised, and with that predicted by the quantum theory; also, the requirements of the isotope effect are completely satisfied. Hence the heads must be considered genuine. Their marked loss of conspicuousness under high dispersion is probably due to the close packing of the heads. This must result in the presence together at most points in the spectrum of series of structure lines from a number of different heads. When, under high dispersion, these are well resolved, the positions of individual heads, where new series begin, are naturally relatively inconspicuous. This is true especially of high-temperature spectra (flame or arc), where the series are prolonged. In active nitrogen the series are usually very short, corresponding to the low actual temperature. This tends to make the heads stand out much more sharply.

[19] The agreement is best brought out by comparing vibrational energy terms E''^n. These can be obtained from the original data or conveniently calculated from the equations of Table 6. Even for the larger values of n'', where $E''^n = 2000$ to 4000 wave-number units, the maximum discrepancy between the energy terms for different systems is 4 units,—provided the comparison is restricted for each system to values of n'' for which bands were actually measured.

initial state energies up to 3 volts in excess of the energy of the final state, be little doubt that this common final state is the normal state of the CuI molecule.

The near-equality of the n' coefficients for the A and D bands may be fortuitous or may indicate a relation between the two initial electronic states involved. The same is true in regard to the C and E bands. The agreement, it should be noted, does not extend to the coefficients of n'^2, at least in the latter case (in the former case the data are inadequate for decision).

The D bands are remarkable in that n' has only the values 0 and 1.[20] Presumably higher values of n' would involve instability of the molecule for the D electronic configuration.

In Fig. 2 the various electronic and vibrational levels revealed by the preceding analysis for $Cu^{63}I$ are arranged on a vertical wave-number scale; the arrangement is like that previously used in the case of BO.[17] At the right, the electron levels (N_0, A_0, ... E_0) and their separations, are indicated. It should be recalled that the plotted values for the levels probably deviate slightly from the true values because the data used refer to heads. For $Cu^{65}I$ (not shown), the various electron levels coincide with those of $Cu^{63}I$, but each set of vibrational levels has a somewhat smaller spacing, in accordance with the equations of Table VI.

It will be noted that in all five CuI systems the vibration frequency is less for the excited than for the normal electronic state. Although the individual bands are not resolved, the fact that they are all shaded toward the red is enough to show (cf Sommerfeld, Atombau and Spektrallinien, 4th ed., chap. IX, §3) that the interatomic distance and moment of inertia are greater, in all five systems, for the excited state than for the normal state of the molecule. The above facts both indicate weaker binding forces for the excited electronic states than for the normal state of CuI. The CuBr and CuCl bands disclose analogous relations for these molecules. The correlation of increased moment of inertia with decreased vibration frequency (or vice versa) when a molecular electron is excited is, as Birge has pointed out, a rule without known exception.[21]

Analysis of CuBr and CuCl Spectra. Most of the strongest CuCl heads (mostly the first head of each group) were arranged by Derichsweiler[5] in two long series (I and II) of approximately equally spaced heads. The same is true of CuBr. In each series the intensity is somewhat

[20] There are one or two doubtful and very weak bands for which, *possibly*, $n'=2$.

[21] R. T. Birge, paper before American Physical Society (abstract No. 23, Phys. Rev. **25**, 240, 1925). The question of intensity distribution with respect to Δn and to n' was also discussed in this paper.

undulating, with two principal maxima. Corresponding members of series I and II form characteristic pairs of heads. In the case of CuI (cf. Table VII below), according to Derichsweiler, series II is nearly absent. The present analysis shows that Derichsweiler's arrangement into series has very little significance. In reality the spectrum of CuBr consists probably of four, that of CuCl of six (one closely double) different systems of bands, in part closely intermingled, giving rise to the appearance of pairs of heads.[18] Preliminary study indicates that, as with CuI, the several systems of each compound have a common final state.

Confirmation of Vibrational Isotope Effect

In the reproductions of Plate I, practically all the $Cu^{63}I$ heads recorded in Tables I-V are marked. The corresponding weaker $Cu^{65}I$ heads are not marked, but many of them can be located by comparison with the tables. It will be seen that they are arranged entirely as would be expected (cf. theoretical diagram, I, p. 129). The $Cu^{65}I$ bands are especially well shown at the low-frequency end of the A system. In the region near the origin of each system, the heads of the two isotopes are of course not resolved. On the high-frequency side of the origin, the $Cu^{65}I$ heads are partially or wholly obscured, each by the shading from the adjacent $Cu^{63}I$ head.

In order to consider the question quantitatively, let us suppose that one of two isotopic molecules emits a system of bands, the wave-numbers of whose origins can be expressed by an equation of the form

$$\nu_1 = \nu^0 + a'n' - b'n'^2 - a''n'' + b''n''^2 \qquad (1)$$

Then for the other isotope, according to theory (I, p. 127),

$$\nu_2 = \nu^0 + \rho a'n' - \rho^2 b'n'^2 - \rho a''n'' + \rho^2 b''n''^2 \qquad (2)$$

Here $\rho = \sqrt{\mu_1/\mu_2}$, μ_1 and μ_2 being the respective reduced masses. In case one has data on band-heads, instead of on origins, small contributions are added to all the terms of Eq. (1); and since these are subject to the *rotational* isotope effect, which differs from the vibrational effect, the relation of ν_2 to ν_1 is slightly altered. In respect to the terms depending on n' and n'', the effect should be negligible (I, p. 132) as compared with experimental error. In respect to the constant term, a small but perhaps appreciable effect is to be expected.[22]

[22] The fact that the data of Tables I-V are on heads, instead of on origins, involves the possibility of a slight shift of all the $Cu^{65}I$ heads with respect to the $Cu^{63}I$ heads. For the constant term of Eq. 1 now represents not ν^0 alone (for which no appreciable isotope effect is to be expected: (I, p. 124-5)), but $\nu^0 + \nu_{head}$, where ν_{head} is the distance from the origin to the head of the band for which n' and n'' are both zero. Corresponding to ν_{head} there must be a rotational isotopic displacement of approximately $(\rho^2 - 1)\nu_{head}$

If ν_1 refers of $Cu^{63}I$, then for $Cu^{65}I$ as compared with $Cu^{63}I$, $\rho = 0.98966$, and $\rho^2 = 0.97943$. From the $Cu^{63}I$ coefficients in the equations of Table VI, the corresponding theoretical values of the $Cu^{65}I$ coefficients can be calculated. The equations so obtained have been given in Table VI. From these the theoretical positions of all the $Cu^{65}I$ heads can be calculated. These predicted values can then be compared with the experimental data. It is most convenient to do this by comparing calculated with observed values of the *isotopic displacement*, $(\nu_2 - \nu_1)$, as is done in Tables I-V. The result is complete agreement, within experimental error, for the entire range of n' and n'' values in all the systems, so far as data could be obtained.[22,23] The slight average deficiency in the observed as compared with the calculated isotopic displacements for the E bands is probably within experimental error, but is in the direction to be expected[22] from the fact that the measurements were on heads. The data are not accurate enough to furnish evidence on the question of half-integral vibrational quantum numbers.[22]

Intensity Distribution in the CuI Bands

In a system of bands, the distribution of intensity with respect to n' and n'' is of interest chiefly from two points of view, distribution with

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(I, p. 131). In the CuI bands, ν_{head} is always positive, since the heads are shaded toward the red. Hence, since $(\rho^2 - 1)$ is negative here, this rotational contribution to $(\nu_2 - \nu_1)$ must be negative; its magnitude, of course, cannot be determined without analysis of the band structure. In the equations of Table VI and the calculated isotopic displacements of Tables I-V, no allowance was made for this contribution. If it is appreciable, it should therefore be evident by an appreciable negative value for the average observed minus the average calculated isotopic displacement.

If, as is apparently true in BO,[17] the true minimum values of n' and n'' are 1/2 instead of 0 as assumed throughout the preceding discussion, the bands here assumed to have $n' = n'' = 0$, and so the constants of the equations of Table VI, should be subject to a vibrational isotopic displacement $(\nu_2 - \nu_1)$ of $+0.28$ units for the A bands, and $+0.18$ units for the E bands. These effects are accordingly of opposite sign to the rotational head effect discussed in the preceding paragraph. The calculated net effects should be: A bands, $+0.28 - x$; E bands, $+0.18 - y$. The observed effects are: A bands, $+0.05$; E bands, -0.4. It will be seen that the observed effects do not contradict the existence of half quantum numbers. The relatively large experimental error, the possibility of relative error, due to differences in intensity, etc., in setting on the heads of the two isotopes, and the fact that x and y are unknown, make it impossible, however, to draw any positive conclusions.

[23] The confirmation of the theory is of course not nearly as exact as in the case of BO,[17] on account of the much smaller values of the isotopic displacements.

In the case of BO, equations for ν_1 and ν_2 were obtained independently from the experimental data, and their coefficients compared. This is a rather more rigorous test than that here applied; but unless the data used are equally complete and accurate for both isotopes, it is one which is likely to disguise somewhat the real agreement with theory.

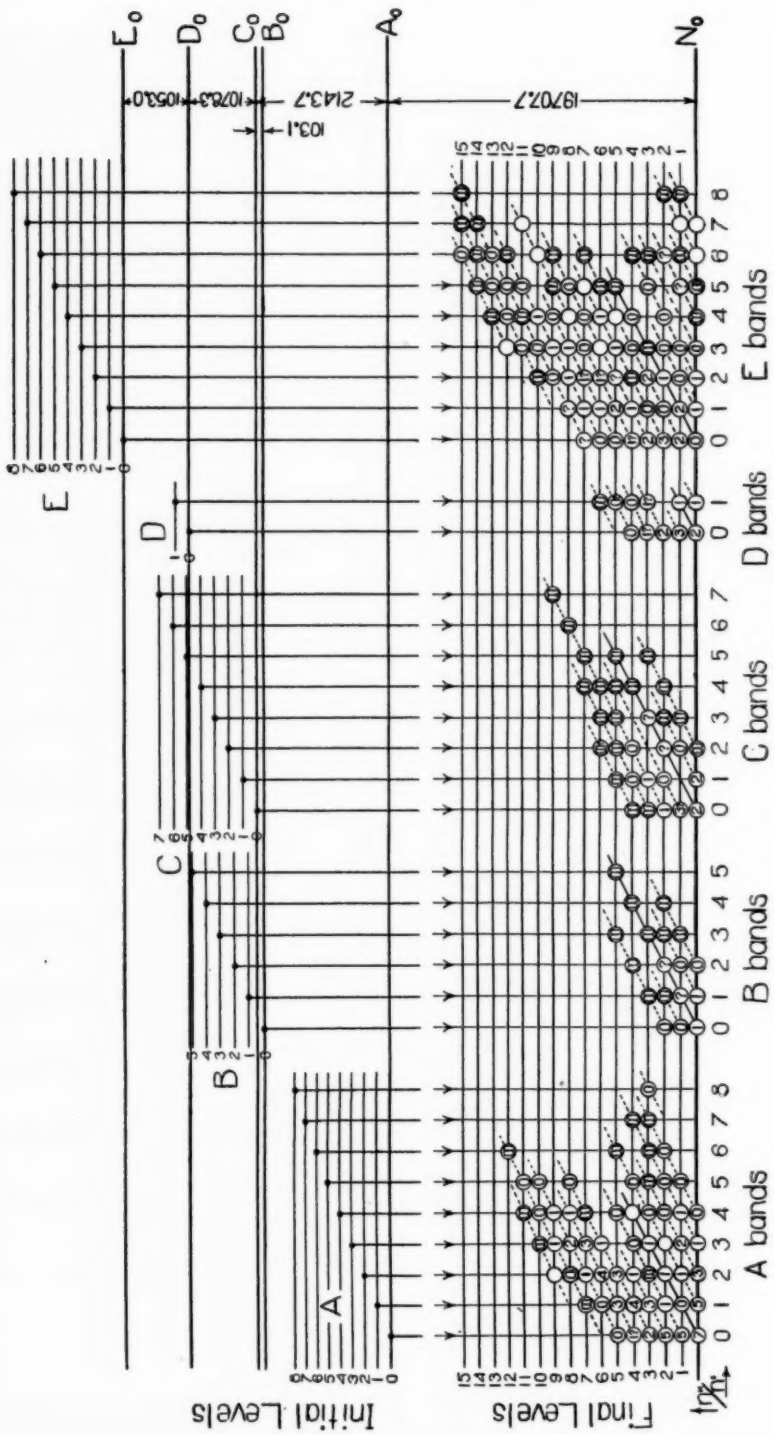

Fig. 2. Energy level diagram for CuI molecule.

Fig. 2. Energy level diagram for CuI molecule.—The electronic and vibrational energy levels found by analysis of the CuI band spectrum are shown on a vertical wave-number scale. Each electronic level (N_0, the normal level, A_0, B_0, . . . , excited levels) is shown by a heavy horizontal line; above it the correlated vibrational levels are shown. In the case of the excited electronic states, the lines for the vibrational levels are drawn only part way across the diagram, in order to avoid confusion. Rotational levels are not shown. The A bands correspond to transitions from A levels to N levels, the B bands to transitions from B to N levels, and so on. Each observed band is indicated by a circle near the lower end of a vertical line, the figure in the circle denoting intensity; where the figure is omitted, the intensity is very low (000). Diagonal lines are used to indicate band-sequences, the full-line diagonal representing the (0) sequence. The spacing of the electron levels is indicated at the right.

respect to Δn ($\Delta n = n'' - n'$), and with respect to n'. The former is a matter of transition probability, depending on several factors recently discussed by Lenz in relation to the correspondence principle.[24] The latter probably depends chiefly on the initial distribution of excited molecules among various n' values, and so gives a means of studying the n' distribution. In the case of CuI, Fig. 2 gives a good idea of these distributions for each of the five systems of bands. Each diagonal line serves to mark out a "band-sequence," i.e., a set of bands of given Δn; each vertical line marks a set of given n'. By comparison of adjacent diagonal or vertical sets, respectively, the Δn or n' distribution can be studied.

For thermal equilibrium, the number N_n of molecules having a given value n of the vibrational quantum number n', and a corresponding energy E_n, should be proportional to $e^{-E_n/kt}$. Assuming, as an approximate average value for the five systems, $E_n = 225n$ (wave-number units), taking k in the same units ($k = 0.698$), and assuming $T = 373°\text{K}$, N_n is proportional to $e^{-0.865n}$. For $n = 0, 1, 2, 3, 4, 5, \ldots$. this gives values of N_n proportional to 1, 0.42, 0.177, 0.075, 0.032, 0.013, ... No more than a rough qualitative comparison is possible with the recorded intensities of Tables I-V and Fig. 2. However, it will be seen that in all five systems there is a steady falling off of intensity from $n' = 0$—except, as previously noted, that the D bands are completely cut off above $n' = 1$—at a rate which seems to be in accord with the preceding calculations, corresponding to a low temperature.

The above result is in contrast to that previously observed[17] in the case of the α and β systems of BO. For BO, E_n is approximately $1260n$, so that the N_n values should fall off very rapidly, in proportion to $e^{-4.85n}$ for equilibrium at 100°C. For $n' = 0, 1, 2, \ldots$. they should then be proportional to 1, 0.0079, 0.00006, ... Actually, the $n' = 0$

[24] W. Lenz, Zeits. f. Phys. **25**, 299 (1924). Cf also T. Heurlinger, Zeits. f. Phys. **1**, 82 (1920).

series are less intense than some of the others, the intensity maximum being near $n'=2$; in addition, bands with n' values as high as 8 were observed, which would obviously be impossible for thermal equilibrium. Non-thermal and high-temperature vibrational energy distributions occur in other cases of band spectra excited by active nitrogen, e.g., in the CN and SiN bands. In the case of the NO β bands (β bands of active nitrogen), as Birge has recently pointed out,[21] the distribution corresponds more nearly to equilibrium at the (low) temperature of active nitrogen. Further discussion of these points will be found in the paper[17] on BO.

The distribution with respect to Δn in the CuI bands considerably resembles that in the β bands of BO. Δn ranges from perhaps -6 to $+9$, and, although there is some approach to the symmetry about $\Delta n=0$ which is predicted by Lenz's theory,[24] there is an obvious preference for positive Δn values.[25] Another characteristic feature, noted here and in both α and β systems of BO, and perhaps typical of band spectra in general,[21] is the tendency for numerically large Δn values to be associated with large n' values. Although Lenz does not refer to it, this effect, as also the preference for positive Δn values, appears to be predictable from his theoretical treatment; for the occurrence of large values of Δn is there connected with the existence of considerable perturbations of the electronic motion by the vibrational motion of the nuclei; and the magnitude of such perturbations must increase with the value of n, which determines the amplitude of vibration. Hence large values of n' should favor large values of Δn, and also, since the motion of the emitting electron in both initial and final states of the molecule must be considered in Lenz's application of the correspondence principle, should favor positive values of Δn, since for these n'' is also large.

The association of large n' with large Δn values has a striking effect on the appearance of band sequences in cases, like those of the copper halides, where the members of a sequence follow one another in close succession (cf. Plate I). In the sequences near the origin, i.e., those for which $|\Delta n|$ is small, each sequence begins with an intense head —for which either n' or n'' is zero—the succeeding heads being progressively less intense.[26] Farther from the origin, the intensity maxi-

[25] This is probably *not* due primarily to variations in plate sensitivity and prism transmission, although of course these must have a marked distorting influence.

[26] Exceptions to this rule of progressive decrease sometimes occur due to abnormally low intensity of particular bands. Thus (cf. Plate I) the $\Delta n=0$ sequence of the E bands starts out with a weak (0,0) head, while the $\Delta n=+1$ sequence has a weak spot at the (1,2) band; again, the A sequence for which $\Delta n=0$ has a weak spot at (1,1), followed by a revival with (2,2).

mum shifts away from the first head, and in the highest-numbered sequences the first few heads may become too weak to be detected (cf. Plate I and Fig. 2, A and E bands). Konen noted this effect in the copper halide bands, and gives a good diagram[4] illustrating it in the case of some of the CuCl bands; certain fluoride bands also show it well. This phenomenon is particularly well marked in the positive sequences (Δn positive). Here the first head of each sequence corresponds necessarily to $n'=0$, whereas in the negative sequences, the value of n' for the first head is necessarily the same as $|\Delta n|$.

Attention may be called to the A bands of CuI as a typical example, with respect to arrangement and intensity distribution, of a well-developed band system. The A bands also illustrate well the abrupt change of spacing for the strong first heads of successive sequences, at the origin of the system. These points appear to good advantage in Plate I on account of the freedom from marked variation of photographic sensitivity and from overlapping by other band-systems, in the region occupied by the A bands. The absence of resolution of the bands into structure lines also helps to make clear the arrangement of the bands.

Comparison with Data of Previous Investigators

Data in the literature on complex band spectra often refer to the first head only of each of the more obvious sequences. This is illustrated in Table VII, where the data of previous observers on the CuI bands are

Table VII

Comparison with previous data

Previous data (wave-lengths)*			Present identification
M.	D.	E.&V.	
5393	———	———	A sequence 5354-5419
5314	———	5330	" " 5282-5364
———	———	5250	?
5232	———	———	A sequence 5211-5241
———	5210(I)	5210	Head 0,2 A, 5210.7
5144	5141(I)	5142	" 0,1 A, 5141.1
———	———	5106	" 2,2 A 5101.9
5073	5072(I)	5075	" 0,0 A, 5072.8
5018	5019(II)	———	" 1,0 A, 5019.7
4959	———	———	" 2,0 A, 4968.3(?)
	4883(II)	———	A sequence 4873-4930
	4826?(II)	———	?
	4769(II)	4760	C sequence 4744(?)
	4710(II)	———	Head 0,2 B, 4711.3
	4686(I)	4685	" 0,2 C, 4686.8 and 4687.8
	4631(I)	4630	" 0,1 C, 4630.6
	4575(I)	4575	" 0,0 C, 4575.2

* M. = Mitscherlich (wave-lengths calculated by Watts in his "Index of Spectra" from photograph by Mitscherlich); D. = Derichsweiler (Roman numerals in parentheses after wave-lengths denote series of Derichsweiler[5]); E. & V. = Eder and Valenta.[3]

TABLE VII—continued

4523(I)	4523	Head 1,0 C, 4527.9
4462(?) (I)	4464	" 0,2 D, 4462.2, and 1,7 E, 4463.6
4409(I)	4408	" 0,5 E, 4408.1
4358(I)	4358	" 0,4 E, 4358.3; 0,0 D, 4360.0; 1,5 E, 4364.0
———	4323	?
———	4320	" 1,0 D, 4320.0
4309(I)	——	" 0,3 E, 4308.2 and 4309.6
———	4280	" 3,5 E, 4280.1
4261(I)	4261	" 0,2 E, 4261.7
4214(I)	4213	" 0,1 E, 4214.6
4169(I)	4172	" 0,0 E, 4168.5 or 1,1 E, 4174.6
4126(I)	4130	" 1,0 E, 4129.4
———	4098	" 2,0 E, 4091.3

compared with the present data. In the higher-numbered sequences, the first head becomes too faint to be noticed, and a rough measurement of the beginning or middle of the region of maximum intensity is likely to be given; obviously such data are of almost no value from a theoretical standpoint.

For the first head of a sequence, either n' or $n''=0$. On the low-frequency side of the origin (n', $n''=0$), in each CuI system, these form a series $(n', n'')=(0, 0)$, $(0, 1)$, $(0, 2)$, ... with a nearly constant first difference of somewhat over 260 wave-number units, common to all five systems on account of their common final electronic state. Derichsweiler's series I for CuI is made up chiefly of the E bands (0, 0), (0, 1), ... (0, 5) and the C bands (0, 0), (0, 1), (0, 2), pieced together by (0, 2) D and (1, 0) C, which, however, of course do not fit in very well (this was explained by Derichsweiler as perhaps due to inaccuracies of measurement). After a gap containing miscellaneous bands grouped as series II, series I reappears with (0, 0), (0, 1), and (0, 2) of the A system.

THE EXCITATION OF SPECTRA BY ACTIVE NITROGEN

The suggestion has been made by several writers[27,28,29] that the excitation of spectra by active nitrogen is the result of "collisions of the

[27] R. T. Birge: cf. abstract, Phys. Rev. **23**, 295 (1924); Nature, Nov. 1, 1924.

[28] R. S. Mulliken, loc. cit.;[7] Nature, Sept. 6, 1924; Phys. Rev. **25**, 278 (1925).

[29] M. N. Saha and N. K. Sur, Phil. Mag. **48**, 421 (1924). It should be pointed out that this paper contains certain errors in the interpretation of the band spectra appearing in active nitrogen, and in the estimated energy of the latter. These have been corrected in Birge's letter [27] to Nature. See also Foote and Ruark, Nature, Nov. 22, 1924, and Foote, Ruark, and Chenault, (abstract, Phys. Rev. **25**, 241, 1925) who discuss the excitation of the spectrum of mercury by active nitrogen. The present writer believes that Birge's estimate of about 11.5 volts, for the energy of active nitrogen in the state which immediately precedes the emission of the characteristic visible afterglow bands, should be reduced to 10.4 volts (this point will be discussed elsewhere). The true energy may be somewhat different, however, probably higher, since the active nitrogen must be in a metastable state[27] which presumably differs from the emitting state, although Birge assumes the two to be identical.

second kind," analogous to the action of excited mercury atoms in the work of Franck and Cario.[30] The effects are, however, much more varied in active nitrogen than with excited mercury atoms. The excitation of atomic spectra by active nitrogen, as studied experimentally by E. P. Lewis[31] and by Rayleigh and Fowler,[32] has been discussed in some detail by Saha and Sur.[29]

The behavior of the copper halides in active nitrogen illustrates particularly two characteristic modes of action of the latter. As indicated in the preliminary abstract,[7] it appears that excited N_2 molecules may either (a) excite molecular electrons so as to give rise to the emission of the halide band spectra, or (b) dissociate the halide molecules. The excitation of atomic spectra is also illustrated, excitation of the copper and halogen atoms possibly accompanying but probably following the dissociation. Another possibility referred to in the abstract, namely reaction with the halide molecule to form copper nitride, must now be regarded as very doubtful (see under "oxide bands" in introduction), although the analogous process occurs in many other cases, e.g.,[33] formation of CN and SiN, respectively, by reaction of N_2' molecules (the prime will be used to denote an excited atom or molecule) with carbon and silicon compounds. Other interesting reactions are the appearance of the NO bands[33] on admission of O_2 or other oxygen compounds into active nitrogen, and of the CN and NO bands (also probable CO bands) on admission of CO. Possible formulations of these reactions are $O_2+N_2' \rightarrow NO'+NO$, and $CO+N_2' \rightarrow CN'+NO$, or $CN+NO'$.

In the case of the copper halides, the occurrence in high intensity of the copper arc spectrum (over 80 lines were identified) and of the intense iodine arc line[34] at λ2062 when CuI was used, indicate that excited Cu

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The subject of active nitrogen has also been discussed by N. R. Dhar (J. Phys. Chem. **28,** 948, 1924).

[30] Franck and Cario, Zeits. f. Physik **9,** 259; **10,** 185; **11,** 161 (1922); **17,** 202 (1923).

[31] E. P. Lewis, Astrophys. J. **20,** 49 and 58 (1904); Phil. Mag. **25,** 826 (1913); and other papers.

[32] Ref. 10 and later papers in Proc. Roy. Soc.

[33] See R. S. Mulliken, Phys. Rev. **25,** 277-8, 290, and references there cited.

[34] C. Füchtbauer, F. Waibel, and E. Holm found this line strongly absorbed in atomic iodine at 1000°C (Zeits. f. Phys. **29,** 367, 1924). Their measured wave-length was $\lambda_{vac.}=2062.1\pm0.1$. An approximate measurement by the writer on the emission line obtained from CuI gave $\lambda_{vac.}=2062.3$. W. Gerlach and F. Gromann (Naturw. **12,** 578, 1924) had previously reported a line at λ2063 absorbed by partly dissociated iodine at 150°C, but their result is less conclusive than Füchtbauer's on account of the probable molecular absorption. A strong emission line at λ2064 reported by O. Oldenberg (Zeits. f. Phys. **18,** 7, 1923), and at 206mμ by Ludlam and West (Nature **113,** 389, 1924), is without doubt identical with that here under discussion. The nature of λ2062 has also been discussed recently by L. A. Turner and K. T. Compton (Phys. Rev. **25,** 791, 1925).

and I atoms are formed in large numbers as a direct or indirect result of process (b) above. Exactly the same set of Cu lines is obtained, with the same relative intensities, so far as could be judged from inspection of the photographs, whether CuCl or CuI is used (and so far as could be seen in a short exposure, the same as with CuBr). According to Dr. A. G. Shenstone, who was so kind as to examine the data, the entire arc spectrum appears to be present, and in addition a group of lines whose initial state corresponds to a slightly negative term, hence presumably to simultaneous excitation of two electrons. The spectrum differs markedly in intensity distribution from that of the ordinary copper arc.

It may be noted that there was no trace, when CuI was used, of the intense band spectrum which is excited when iodine (I_2) is admitted to active nitrogen.

Since CuCl is known to be largely or completely associated to Cu_2Cl_2 in the vapor state[35] (presumably CuBr and CuI also are associated), it is not possible at present to specify definitely the details of processes (a) and (b) above. It is likely that the formation of CuX′ molecules and Cu′ and X′ atoms by the interaction of N_2' molecules and CuX or Cu_2X_2 molecules occurs in a number of different ways. The category of possible modes of dissociation and excitation is of course limited to processes in which the expenditure of energy does not exceed the initial energy of the N_2' molecule (plus a small contribution due to energy of relative translation of the impinging molecules); this initial energy corresponds probably to 10.4 volts or a little more.[29]

The formation of CuX′ molecules might occur directly from Cu_2X_2 and N_2', or might require the intermediate formation of unexcited CuX molecules. Similarly the formation of Cu and X atoms from Cu_2X_2 might occur in one or in two steps, and the formation of Cu′ and X′ atoms in from one to three steps. In any case there are three distinct possibilities as to the mode of excitation of the Cu and X atoms: (1), the dissociation of Cu_2X_2 or CuX molecules may yield neutral unexcited atoms, excitation of these occurring in subsequent impacts with N_2' molecules; (2), excitation may occur simultaneously with dissociation; (3), the dissociation may yield the ions Cu^+ and X^-. Since the ionization potential of Cu is about 7.7 volts, the energy of N_2' is considerably more than enough for the excitation of the entire arc spectrum of Cu in secondary impacts of Cu with N_2' in connection with (1); further, the excited spectrum should be the same for all three halides, as is the case for the observa-

[35] See von Wartenberg and Bosse, Zeits. f. Elektrochem. **28**, 384 (1922).

tions reported above. In process (2) the energy required includes a heat of dissociation in addition to the energy of excitation. The heat of dissociation may be estimated[36] at 2 or 3 volts for CuX, so that excitation of the entire arc spectrum might still be possible. It would, however, be strange if there were not then differences in intensity distribution, contrary to the observed facts, for the different halides. Dissociation of Cu_2X_2 in any manner, with simultaneous excitation of Cu atoms to give the entire arc spectrum, must probably be ruled out on account of the large energy required for dissociation.[36] Process (3), followed by reunion of an electron with a Cu^+ ion, should like process (1) give the same Cu spectrum for all the halides, in accord with observation. The energy required for (3) would not be excessive[37] for dissociation of CuX, but might be too great for the reaction $Cu_2X_2 \rightarrow CuX+Cu^++X^-$. On the whole, the evidence is decidedly against (2), and in favor of (1) or (3), as the main factor in the formation of excited Cu atoms. Energy considerations favor (1) as against (3) if the dissociation of Cu_2X_2 occurs in one step; the fact that the system $Cu+X$ has less energy than Cu^++X^- also indicates it to be a more likely result of dissociation. For the formation of X′ atoms only (1) is possible.

The increasing relative intensity of the Cu line spectrum, as compared with the CuX band spectrum, in going from CuCl to CuI, may be ascribed to an increasing probability of dissociating rather than exciting the CuX molecule, correlated with the decreasing chemical stability of the molecules in this order.

There is a possibility that CuX_2 molecules may be important in the excitation of the spectra of the Cu halides by active nitrogen, although

[36] Assuming that all three cuprous halides are present in the vapor state chiefly as double molecules, the following approximate values for the heat of dissociation into unexcited neutral atoms can be calculated from thermochemical[35] and electron affinity data: Cu_2Cl_2, 10.2 volts, Cu_2Br_2, 9.1 v, Cu_2I_2, 8.3 v, using the value 68 kg.-cal. per mol for the heat of vaporization of Cu (cf R. W. Millar, Ind. Eng. Chem. **17,** 34, 1925). The heat of dissociation of CuX into atoms and of Cu_2X_2 into 2 CuX are unknown, but may be estimated by assuming that the former is the same as for AgX (which does not form double molecules in the vapor state). The writer is indebted to Dr. R. H. Gerke for this suggestion. For AgCl vapor, the heat of dissociation into atoms is equivalent to about 3.3 volts, for AgI to about 2.2v (cf. R. H. Gerke, J. Am. Chem. Soc. **46,** 953, 1924; also von Wartenberg and associates, Zeits. f. Elektrochem. **27,** 162, 568, 1921, and **28,** 284, 1922). Assuming the same values for CuCl and CuI, the heat required for $Cu_2X_2 \rightarrow 2CuX$ is then equivalent to 3.6v for CuCl and 3.9v for CuI.

[37] Gerke (l.c.[36]) points out that for halogen salts the heat of dissociation is approximately equal to the electron affinity of the halogen. A corollary of this is that the heat of dissociation of such salts into ions must be about equal to the ionizing potential of the metal.

the weight of chemical evidence indicates that CuX_2 is decomposed to Cu_2X_2 and X_2 in the process of vaporization. In the present work, both $CuCl_2$ and Cu_2Cl_2 were used, but no obvious differences in relative intensities of different bands, or of the bands as compared with the Cu lines, were observed.

Mercury halides. Some experiments of the writer on the excitation of spectra of certain volatile salts by active nitrogen are of interest here. PbI_2, HgI_2, and $HgBr_2$ have been tried.[38] Each gives the arc spectrum of the metal, well developed, also λ2062 and other I arc lines[38] in the case of the iodides, and characteristic halide bands in each case (very weak in the case of PbI_2, strong in the other two cases). The band spectra appear to be rather complex, suggesting triatomic emitters MX_2, but it seems more likely that they are due to diatomic emitters MX, in which case the complexity may be due to the presence of several superposed systems of bands as in the CuX spectra. In the case of the two Hg salts, the complete arc spectrum of Hg appears to be developed; thus diffuse series lines are present at least up to $2p_1-6d$; the 6d terms correspond to an energy of 10.0 volts, only 0.4 v short of ionization. In both cases the intensity distribution appeared to be closely similar to that in other experiments where Hg alone was used (except that λ2537 was relatively much weaker in the latter case, presumably because of greater absorption).[38] These results parallel those with CuCl and CuI, and lead to similar conclusions, except that process (1), dissociation into unexcited atoms, is even more definitely indicated here, on account of the high ionizing potential of Hg, as the chief factor. The formation of Hg^+ ions, probably by the reaction $Hg+N_2' \rightarrow Hg^+ + N_2 + e$, is indicated by the (rather weak) presence of the Hg spark line λ1942 (the emission of this line would follow the secondary process $Hg^+ + N_2' \rightarrow Hg^{+\prime} + N_2$).

The study of the excitation of spectra by active nitrogen is being continued, and a further discussion will be given later.

[38] In some of the experiments with the iodides, the characteristic banded structure beginning near λ3450, which results[10] from the action of N_2 (or a suitable electrical discharge) on I_2, was present. This was probably due to partial decomposition of the iodide before its entrance into the active nitrogen, or in part to secondary formation of I_2 from I atoms, rather than to direct formation of I_2 or I_2' molecules by dissociation. The spectrum of HgI_2 in active nitrogen was earlier examined by Rayleigh and Fowler[10], who found this iodine band fairly prominent. Of the Hg line spectrum, they noted only λ2537; this result was probably due to an exposure insufficient to bring out the other lines, since in the present work λ2537 was found to be much more prominent than the latter.—In the present work with the iodides (and iodine) several additional lines, evidently iodine arc lines, were noted (cf. abstract of paper by R. S. Mulliken and L. A. Turner, Phys. Rev. **25**, 886, 1925).

Nature of Excited Electronic States in Copper Halide Molecules, and the Band Spectra of Polar Compounds

The nature of the electronic changes involved in the excitation of the CuX molecule (X = any halogen) will now be considered briefly. Since CuX is of a polar or ionic type—although less definitely so than compounds like NaCl—the excited electron must probably belong either to the Cu^+ ion or to the X^- ion. Excitation of an X^- electron in Cu^+X^- by impact with a free electron or excited atom or molecule would presumably mean complete loss of this electron to the Cu^+ ion, since outer quantized orbits are hardly to be expected for this electron in the X^- ion. The Cu atom would thus be left in its normal state, or, if enough energy were supplied, in one of several excited states; and the Cu and X atoms would be left clinging together by virtue of secondary forces as a non-ionic molecule CuX. From this condition they might undergo, as the result of the impact of a third molecule, either the change $CuX \rightarrow Cu + X$, or (cf. Born and Franck, ref.[39]) $CuX \rightarrow Cu^+X^-$. The spontaneous occurrence, with the emission of a band spectrum, of the reaction CuX or $Cu'X \rightarrow Cu^+X^-$ is conceivable, but must probably be ruled out.[39] Another possibility is that, in the presence of a Cu^+ ion, the I^- ion would be so greatly deformed that a series of quantized states for an I^- electron could occur, resembling those in an I atom. It is more probable, however, that the observed group of five electron levels in the CuI molecule corresponds to excitation of the Cu^+ ion. The five CuI band-systems should then be analogous to the most easily excited lines of the Cu^+ spectrum. This spectrum should contain odd-numbered multiplets. The group of CuI levels A_0 to E_0 might then correspond to a multiple term of Cu^+, considerably modified, of course, and perhaps increased in complexity, by the presence of the I^- ion.

That the Cu^+ ion contains an easily excited electron or electrons is indicated by the existence of salts in which the Cu atom has a valence of two, showing that the Cu^+ ion in Cu^+X^- has an electron which is easily transferred to a halogen atom to form $Cu^{++}X^-_2$. The process of complete transfer of a Cu^+ electron to an X atom is of course markedly different from the mere excitation of a Cu^+ electron in Cu^+X^-; it may be described as an induced ionization, being assisted by the electron affinity of the X

[39] M. Born and J. Franck (Ann. der Physik, **76**, 229, 1925) have concluded that the emission of radiation in such a process is, on correspondence principle grounds, not to be expected. The same would apply to the converse process of excitation of the molecule by absorption of radiation. See also their important article in Zeits. f. Phys. **31**, 411 (1925).

atom. Excitation of a Cu^+ electron in Cu^+X^-, and complete transfer as in $Cu^+X^- + X \rightarrow Cu^{++}X^-_2$, stand, however, in much the same relation as excitation and ionization of an electron in a single atom. Since in general low ionization potentials involve low resonance potentials, the above correlation of CuX_2 formation with CuX excitation seems justified.

In the same connection it is noteworthy that the halides of those metals which show a valence only of one give no electronic band spectra. In this class are the halides of the alkali metals (and hydrogen).[40] The absence of a valence of two in these cases must depend mainly on the absence of a low enough ionization potential for the positively charged ion (M^+) of the metal. It is especially notable that silver, which belongs in the same group of the periodic system as copper but fails to show a valence of more than one, also fails[40] to give halide band spectra. Gold, also in the same group, shows valences of one and three, and gives halide spectra. It may be that in polar compounds the molecule is incapable of carrying electronic energy much in excess of the heat of dissociation into atoms, any attempt to impart larger amounts of energy resulting, either spontaneously, or as an indirect result of the formation of an excited molecule of a type highly sensitive to encounters with other molecules, in prompt dissociation.[41] The heat of dissociation into atoms corresponds to between 3 and 6 volts for the various alkali and hydrogen halides (being least for the iodides and for the hydrogen compounds), and probably to between 2 and 5 volts for the three cuprous halides.[36,37] The observed band systems of the Cu halides probably all correspond to electronic excitation energies lying between 2.4 and 3.1 volts;[42] for the five CuI systems the figures are 2.44, 2.68, 2.70, 2.83, and 2.96 volts. The complete absence of ultraviolet band spectra in the Cu halides, and of *all* electronic band spectra in the other halides mentioned, can both, then, be accounted for by the suggestion above in regard to instability of energized molecules.[43]

[40] There appears to be no record whatever in the literature of electronic band spectra for these compounds, in spite of much investigation.

[41] In the case of non-polar compounds such as H_2, N_2, and I_2 it is, however, of course well known that the molecule can possess electronic energy greatly in excess of the heat of dissociation, and can lose this excess energy in band spectrum emission.

[42] This is definitely shown for CuI by the preceding analysis, and is also probably true for CuBr and CuCl.

[43] A possible alternative explanation of the absence of observed band spectra in the compounds mentioned is that they lie wholly in or below the Schumann region. It seems unlikely, however, that this would be consistently true for all members of the class, and that, in addition, no jumps between higher levels would occur giving rise to bands in the visible or ordinary ultraviolet. Also, in recent unpublished work of Dr. L. A. Turner on a mixture of H_2 and I_2, no bands attributable to HI were found in the Schumann region. The occurrence in positive rays of such ions as $(HCl)^+$, $(NaI)^+$, $(HgI_2)^+$, etc., suggests

If MX molecules are unable, on account of the absence of an easily excited electron in the ion M^+, to give electronic band spectra, one would naturally expect the same to be true of MeX_2 molecules, where Me is one of the alkaline earth metals; for the Me^{++} ion, like the M^+ ion, contains no easily excited electron.[43] As a matter of fact, all the members of this group give band spectra, in the visible and near ultraviolet, with ease; the fact that many of these can be obtained in the Bunsen flame shows that the electronic energy of the emitting molecule is relatively small, the band emission being in all probability accompanied by a return to the normal state of the molecule. These facts obtain a simple explanation in harmony with preceding considerations if one attributes these bands to compounds Me^+X^- present in small amounts. Such compounds contain one unused valence electron which should be very easily excitable, much like the single valence electron in an M atom. The excitation of MeX spectra by adding MeX_2 to a flame would then be completely analogous to the excitation of M spectra by the addition of MX to a flame (e.g., the excitation of the sodium D lines by adding NaCl to a flame). There is little evidence for compounds of the type MeX in the solid state,[44] but their existence in the vapor state is to be expected, in small amounts in equilibrium with MeX_2 and Me molecules. Such molecules would considerably resemble BO and CN (also SiN); all are "odd molecules" containing a single unused and presumably easily excited valence electron; it may be recalled that in a previous paper[33] considerable evidence was presented for the existence of an analogy between BO and CN and the Na atom. The structure of the spectra of the alkaline earth halides appears to be in agreement with the suggestion that they are due to diatomic molecules, although further investigation is needed. Also, these spectra are characterized by electronic doublets whose separation is of the same order of magnitude as, and which may well be analogous to, those of the spark spectra of the corresponding alkaline earth metals and of the arc spectra of the adjacent alkali metals.[45]

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of course, that these should give electronic band spectra, but it should be remembered that a molecule which has completely lost an electron may be stable even if the same molecule with this electron in a highly excited state is unstable.

[44] But cf. refs. given in J. W. Mellor's "Treatise on Inorganic and Theoretical Chemistry," Vol. III, p. 713; also cf. stability calculations by H. G. Grimm and K. F. Herzfeld, Zeits. f. Phys. **19**, 141, 1923.

[45] The spectra of the alkaline earth halides contain each apparently two or more band-systems. The spectra of the chlorides, bromides, and iodides of Ca, Sr, and Ba are closely homologous, as was shown by Olmsted (C. M. Olmsted, Dissertation Bonn, 1906; Zeits. wiss. Phot. **4**, 255-333, 1906). In each case Olmsted investigated particularly one complex system, of homologous structure and similar position for all these

The occurrence of MH, M_2, and similar spectra is not in contradiction with the preceding considerations, which deal with molecules of a polar type; for the types MH and M_2 are probably analogous to the non-polar molecule H_2 or are loose compounds whose electrons are bound in orbits which do not differ radically from those of the same electrons in the unshared atoms, so that these electrons are capable of being excited, with varying degrees of ease, without causing the molecule to become highly unstable.[41,46] The characteristic emission of band spectra by molecules of the supposedly polar type $Me^{++}O^{--}$ is less readily explained, but may be ascribed to an approach to the non-polar type by reason of the expected very marked deformation of the O^{--} by the Me^{++} ion; or, the emission of the bands may be due to a form of the oxide molecule which may be written $Me^{+}O^{-}$. The band spectra of the halides of Zn, Cd, and Hg probably resemble those of the alkaline earth halides, but the less polar character of the compounds, especially those of Hg, favors the existence of MeX_2 in addition to MeX bands.[43] Further study is being made of the points touched on above.

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February 17, 1925.

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halides. These bands appear to be rather similar to the CuX bands, except that the shift of the intensity maximum, in successive sequences on either side of the intense band-group which is presumably $\Delta n=0$, away from the first head of the sequence, is here much more rapid. Assuming $n'=0$, $n''=0$ for the most intense band, the bands for each compound can be expressed by quantum theory formulas of substantially the usual type: $\nu=\nu^e+(a'n'-b'n'^2)-(a''n''+b''n''^2)$. Here $\nu^e=A_1$, A_2, B_1, or B_2, constituting an electronic multiplet. There is a major doublet separation B−A, which increases with the atomic weight of the metal and of the halogen and is of the same order of magnitude as that of the $2p$ terms for the corresponding Me^+ or M spectrum, and a minor doublet separation $A_2-A_1=B_2-B_1$, which decreases with increasing atomic weight of the metal or halogen. It may be recalled that similar double doublets appear in the α bands of BO, the γ bands of NO, etc. The coefficients a' and a'', representing molecular vibration frequencies, are comparable with those of the Cu halides, and decrease, as might be expected, with increasing atomic weight of Me and of X. The positive sign of the coefficient of n''^2 (which it seems impossible to avoid by any other reasonable assignment of vibrational quantum numbers) is not contrary to theory, although it differentiates these bands from all others hitherto analyzed.

[46] For further discussion of hydride bands, see R. S. Mulliken, Phys. Rev. **25**, 509, 1925. In CuH, and, as suggested to the writer by Dr. W. W. Watson, in MeH, it may be that the first valence electron is engaged in a non-polar bond with the H electron, while the second behaves as in CuX and MeX.

SHORT-LENGTH TUNGSTEN ARC CHARACTERISTICS

By S. H. Anderson and G. G. Kretchmar

Abstract

The method used was a dynamical one. Oscillograms were taken giving the current through the arc and the p.d. across the electrodes (4 mm in diam.) as the latter were uniformly separated. This was accomplished by connecting the cam which separated the electrodes directly to the shaft of the oscillograph drum so that the exposure on the film was made while the arc gap was being lengthened. From the measurements of the oscillograms, curves are plotted giving p.d. as a function of current for constant gap length of from 0.005 mm to 0.4 mm, also curves giving p.d. against gap length for different constant current values from 2 to 12 amp. The intercepts of these latter curves on the voltage axis give the "minimal length" characteristic. It is found that (1) for an arc length 0.4 mm, and for shorter gaps where the current is 4 amp. or more, the characteristics are expressed by Nottingham's equation, $E=A+B/i^n$ where $n=1.49$; (2) the value of n for tungsten fits roughly the linear relation of n to the absolute temperature of the boiling point of the anode material, suggested by Steinmetz; (3) the minimal length characteristic is expressed by $E=13.2+1.05/(i-1.75)$, which makes it possible to compute the constants of an ignition or relay circuit so as to eliminate sparking between tungsten contact points.

I. Introduction

THERE has been renewed interest recently in the investigation of the characteristics of electric arcs for two reasons. (1) Information regarding the processes of ionization and values of ionizing potentials have become available so that a more detailed theory of the arc is possible; (2) a knowledge of the characteristics of arcs between metallic contact points is necessary in order to calculate the current potential-difference relations which occur upon opening circuits, such as the primary of an induction coil or an ignition circuit or a relay. K. T. Compton[1] has fully discussed the theory of the electric arc. Nottingham[2] has investigated the characteristics of a number of metallic arcs (copper in particular) and has extended the empirical equation of Ayrton. H. E. Ives[3] has shown the importance of the "minimal length" characteristics of arcs in computing the current potential-difference relations occurring in the discharge as contact points are opened, and has determined these characteristics for gold and platinum. Of all materials used for contact points tungsten is

[1] K. T. Compton, Phys. Rev. **21**, 266 (1923).
[2] Nottingham, J. Am. Inst. Elec. Eng. **42**, 12 (1923).
[3] H. E. Ives, J. Franklin Inst. **198**, 4 (1924).

the most common, and apparently the most satisfactory yet found. So it is highly important to have information of the characteristics of arcs between tungsten electrodes.

II. Method and Experimental Arrangement

The method used was a dynamical one. By means of an oscillograph a record was obtained of the current and the potential difference across tungsten contact points as they were uniformly separated. Fig. 1 shows some of the details of this method. An interrupter housing from a Bosch automobile ignition system was mounted on the frame of the oscillograph so that the cam operating the interrupter lever L could be directly con-

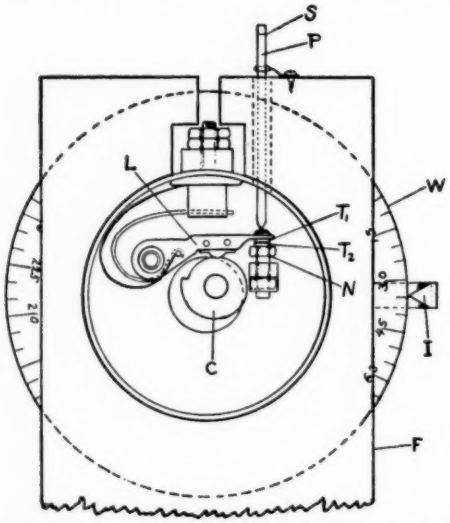

Fig. 1. Arrangement used to separate the tungsten contacts at a uniform rate.

nected to the shaft of the oscillograph drum. The cam C was made specially for this work. It was cut in the form of an Archimedean spiral so that for each revolution the contact points opened once. In operation the cam rotated against the fiber friction block of the interrupter lever, thus separating the contact points T_1, T_2 and producing a gap which could be predetermined from the form of the cam and the angular position. By means of a screw N and lock nuts the interrupter lever could be adjusted to secure proper bearing against the cam. The contact points were 4 mm in diameter, with the contact surfaces flat and carefully polished. Before each oscillogram was taken the surfaces were renewed.

The maximum separation produced was about 0.5 mm and was produced by a rotation of 225° after the initial separation, or in other words, the curves on the oscillogram were distributed over 225/360ths of the

film length. The circular scale W marked in degrees was attached to the drive pulley on the shaft to give the angular position of the cam while making the calibration. The opening of the contact points was indicated by the motion of the pin P which rested on the interrupter lever just above T_1. The movement of P was read by a micrometer microscope.

Fig. 2 is a diagram of the electric circuits. The current through the arc was recorded on the oscillogram by means of a standard vibrator V_1 used in connection with the usual external shunt arrangement for current measurement. Three shunts were provided, each allowing a deflection of about 6 cm on the film for its rated capacity. The capacities were 5, 10, and 15 amp. respectively.

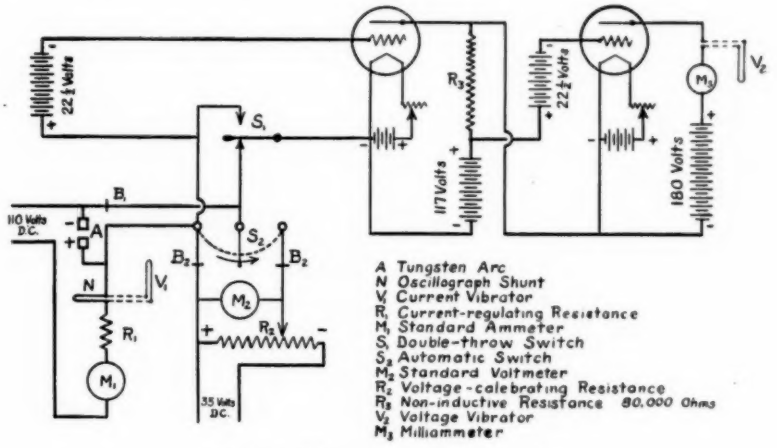

Fig. 2. Diagram of electric circuits

The voltage curve was taken simultaneously with the current on the same oscillogram, by means of a high sensitivity vibrator V_2 and a thermionic tube relay. The thermionic tube arrangement was used in order to give an electrostatic measurement of voltage, so that no current would be diverted from the arc for energizing the voltage vibrator. It consisted of a U.V.201A tube in combination with a Western Electric V.T.2. These were resistance coupled, and the resistance as well as the grid and plate voltages of the tubes were adjusted by trial, so as to give very little deflection for the first 10 volts, and to spread the voltage range from 10 to 30 volts over as great a distance on the film as possible. The values of resistance and voltage used are shown on the diagram.

Oxidation of the tungsten was reduced to a minimum by allowing the current to flow through the arc for about one-half second only, while the exposure was being taken. This was accomplished by means of an auto-

matic switch S_2 which was connected across the arc terminals and was opened simultaneously with the shutter by means of an electromagnetic arrangement. A hand-operated switch (not shown in the diagram) was also connected across the arc terminals, and this was closed, shorting the tungsten contacts again immediately after pulling the string which opened the shutter of the oscillograph. The interval between the opening of the automatic switch and the closing of the hand switch was equivalent to about 3 revolutions of the cam and film drum, as the speed of the drum was about 400 r.p.m. throughout the tests.

The current for the arc was taken from a 110 volt storage battery and adjusted to the proper value by means of the usual regulating resistance in series. The external voltage was maintained at 110 volts throughout the tests. The oscillograph motor and field coils were supplied with 110 volts d.c. from the laboratory motor-generator set.

III. Calibration and Operation

Before making any oscillograms, accurate calibrations of the current vibrator and external shunts were made. This was done by sending the current through a standard ammeter in series with a regulating resistance and the shunt undergoing calibration. The deflection produced by the oscillograph vibrator on the ground glass was then carefully marked for a series of current values through the shunt, taking from three to five readings for each shunt. The deflections were then carefully measured and the resulting current-deflection curve was drawn as a calibration curve for the shunt. This was checked by the straight portions of the current curves on the final arc oscillograms.

The standard ammeter was checked with a potentiometer and standard cell, and was found to be correct within from 1/4 to 1/2 percent over the range used.

It was early apparent that the factors which would limit the accuracy of the work were (1) the measurement of the very small arc lengths, and (2) the oxidation of the tungsten contacts. The tungsten points were always carefully adjusted so that their flat surfaces made a close well-fitting contact. Each renewal of tungsten points made necessary a new calibration of the cam setting. The cam was set to open at the same point for each of the films. The calibrations were made by reading the gap width for each 15° for the first 75°, and then for each 30° up to the maximum value of the cam lift at 225°. This work was always carefully done in duplicate and the curves always showed a good agreement, the variation being less than .01 mm between the two sets of readings. To make sure that oxide was absent, new tungsten contacts were installed for

each value of arc current used, except in a few cases where the same contacts were used the second time when a small current had been used at first which did not appreciably oxidize the tungsten.

The voltage calibration data were obtained by running calibration oscillograms. Because of the possibility of variation of the high voltage dry batteries used for the plates of the tubes, it was thought best to take these before, after, and during the operation of taking the arc oscillograms. This was accomplished easily by a special system of wiring which is shown in Fig. 2. When running a calibration oscillogram the arc was disconnected at B_1, and the automatic switch connected to the potentiometer resistance R_2 through the connections B_2. The standard laboratory voltmeter was connected across the potentiometer resistance at M_2. Each calibration line was obtained by setting the automatic switch in the open position, and adjusting the resistance R_2 until the meter M_2 indicated the voltage desired. The oscillograph shutter was then opened, closing the circuit through the automatic switch at the same time, thus throwing the voltage indicated on M_2 against the constant negative grid bias of the first tube, and giving a line on the film corresponding to the applied voltage. The switch S_1 was kept closed on the side of the $22\frac{1}{2}$ volt negative grid bias all the time of making the calibration, except during the time of taking the exposure, thus keeping the continuous output of the tubes down to a safe small value. Table I shows the average measurements taken from four calibration oscillograms.

TABLE I

Average measurements for voltage calibration curve.
Taken from oscillograms Nos. 4, 8, 11, 14 at positions 10° to 155°

Voltage	10°	32°	81°	120°	155°
0	0				
10	.10	.11			
12	.43	.43			
13	.73	.73			
14	1.07	1.07			
15	1.31	1.31			
17	1.69	1.69	1.69	1.67	1.67
19	2.34	2.33	2.33		
20	3.07	3.07	3.06	3.05	3.04
21	3.54	3.55	3.53	3.53	
23	4.16	4.15	4.14	4.12	4.11
25		4.54	4.52	4.50	4.48
26		4.74	4.72	4.72	4.70
30		5.36	5.34	5.32	5.30

The data of Table I show the effect of the space charge. The space charge seemed to exercise a reservoir effect giving slightly augmented values of the tube output until the excess electrons were used up, which occurred, for a speed of 400 r.p.m., after the drum had traveled 150°.

The effect was observable only for the larger voltage values used, appearing as a slight increase in the amplitude of the calibration line for voltages above 20 volts, and on the first part of the film record. The effect was taken into account on the calibration curve.

The operation of making an arc film was as follows. (1) The new tungsten points were properly adjusted and the cam setting calibrated. (2) The automatic switch was closed, thus short-circuiting the arc. (3) The oscillograph arc light was started and the adjustment of the vibrators tested. (4) The oscillograph shutter was set. (5) The thermionic tube filament currents were turned on and adjusted to the proper values by means of the ammeters in the filament circuits. (6) The film drum was attached and the motor started. (7) Exposure was made for the zero lines. (8) The current through the arc was adjusted to the value desired

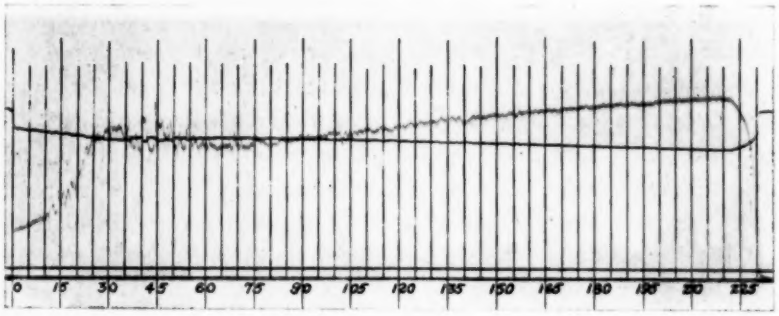

Fig. 3. Typical oscillogram and scale.

and the value recorded as observed on the standard meter M_1. (9) Making sure that the arc light was burning satisfactorily and that the tube filaments had remained constant, the shutter string was pulled making the exposure and then the hand-operated switch was closed. (10) The circuits were all opened and the film developed.

A typical oscillogram is shown in Fig. 3 which shows a film taken with the 5-ampere shunt and an initial current of 3.8 amp. The ruled scale shows the form used under the oscillograms during measurements.

IV. Results

1. *Arc characteristics.* In Fig. 4 are shown the arc characteristics obtained by plotting the potential difference against current. The lowest curve is the "minimal length" characteristic, obtained as described below. From this set of curves potential differences corresponding to different gap lengths for a constant current value were read off and plotted in

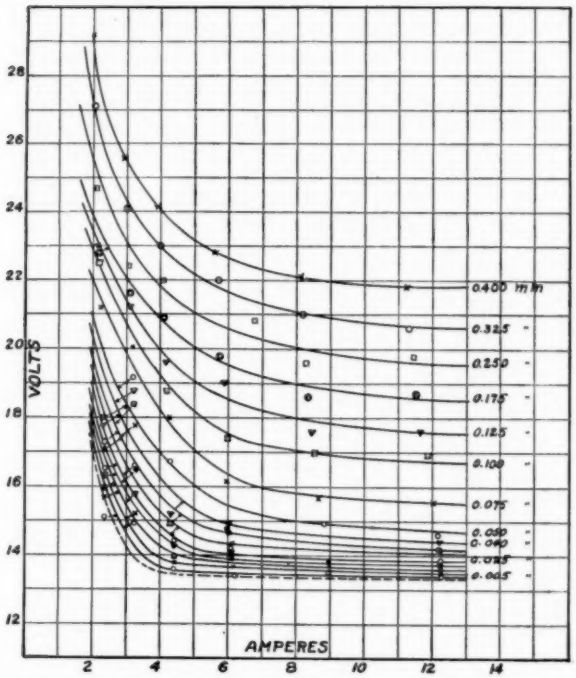

Fig. 4. Arc characteristics for constant length.

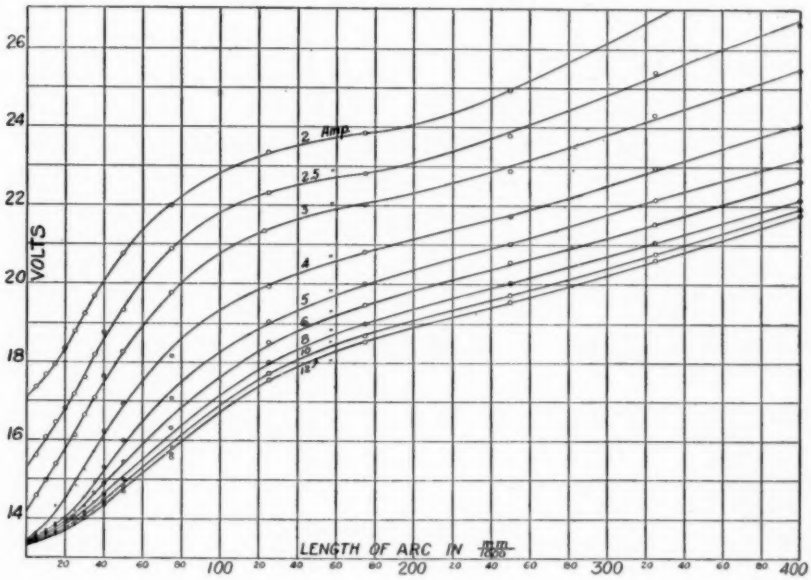

Fig. 5. Characteristics for constant current.

Fig. 5. It is interesting to note that while the general form of the curves in this set is similar to that found by other observers (for example Nottingham), the lower portion shows an upward inflection. This method has made it possible to obtain data for smaller gap lengths than previously reported, so that the intercepts of these curves on the voltage axis are given with considerable certainty. These intercepts, which are potential differences corresponding to currents of 2, 4, 6, 8, and 10 amp. respectively for zero arc length, were read off and plotted in Fig. 4 as the dashed line. *This is the "minimal length" characteristic for the arc between tungsten electrodes.* The convergence of the curves of Fig. 4 to the dashed curve is in agreement with the observation of Ives[3] for gold and platinum, that "the minimal length characteristic . . . . is obviously a member of the family of finite length characteristics."

2. *Equation for arc characteristic.* Nottingham[2] has proposed the following empirical equation for arc characteristics

$$E=A+B/i^n$$

in which E is the potential difference across the arc, i the current, A and B constants for a given arc length and electrode material, and n a constant characteristic of the material but independent of the length. This may be considered a more general form of the equation found by Mrs. Ayrton[4] to hold for carbon arcs. The constants of this equation can be evaluated only by a semigraphical method.[5] Values of A were found for ten gap lengths from 0.4 mm to 0.03 mm, and then log $(E-A)$ plotted against log i (Fig. 6). For two larger gaps, 0.4 mm and 0.325 mm, the points are uniformly distributed about a straight line and the two lines are nearly parallel. So we may conclude that for gaps of the order of 0.4 mm (and probably larger) Nottingham's equation holds for the tungsten arc in air. The slopes of these lines gives the value of n. The average for the two upper lines is 1.487. For gaps smaller than 0.325 mm the upper points depart considerably from a straight line, but the lower points ($i>4$ amperes) lie very close to a straight line parallel to those of the larger gap. Using the straight portion of the first five logarithmic graphs, the average value is nearly the same, 1.48. An inspection of Fig. 4 suggests that, while the lower curves differ in form from the upper, the whole set is one family of curves and it should be possible to find an equation which would hold for all. However, an attempt to do this will be

[4] Hertha Ayrton, The Electric Arc, The Electrician Printing and Publishing Co., London, 1902.

[5] Lipka, Graphical and Mechanical Computation, John Wiley & Sons, New York, 1918, p. 140.

deferred until a redetermination of the characteristics is made with greater precision. In the present work the possible error in the potential difference is ± 1.0 volt which makes the exact form of the curves rather uncertain.

3. *Equation for minimal length characteristic.* Ives found that the minimal length characteristics for carbon, gold, and platinum can be satisfactorily represented by the following equation

$$E=a+\gamma/(i-c).$$

Furthermore, this equation is well adapted to the calculations involved in determining the constants of a circuit such that the arcing is a mini-

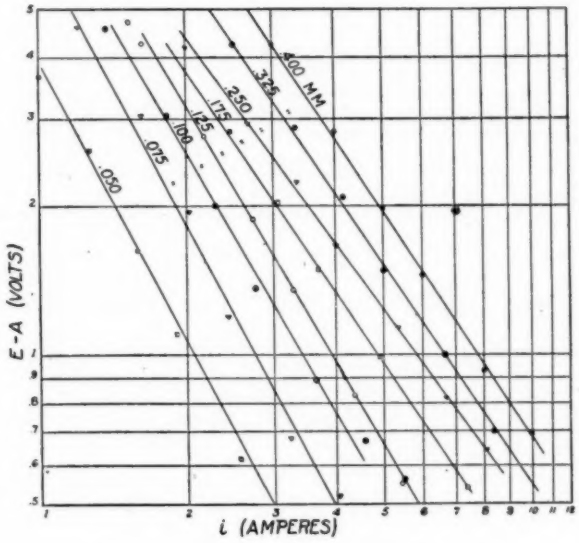

Fig. 6. Log $(E-A)$ as a function of log i.

mum at the opening of contacts. Within the limits of experimental error this equation will also serve for the tungsten minimal length characteristic, the equation after determining the constants being given by

$$E=13.2+1.05/(i-1.75).$$

From this it is seen that *the arc will not persist when the current is 1.75 amperes or less, no matter what potential difference is applied at the electrodes.* This agrees with observations made for small current values. No oscillograms of a persisting arc were obtained when the initial current was less than the above value.

4. *Relation of* n *to the temperature of the boiling point of the electrode metal.* Steinmetz[6] suggested that the temperature of the vapor in the arc is a constant depending upon the boiling point or sublimation point of the material of the anode. Nottingham, following out this suggestion, proposes that the constant n of his equation is a linear function of the absolute temperature of the boiling point or sublimation point of the material of the anode, and obtains a table of values that fit a straight line very well. However, for the anode of aluminum, cadmium, and zinc respectively he uses the boiling point of the metallic oxide rather than

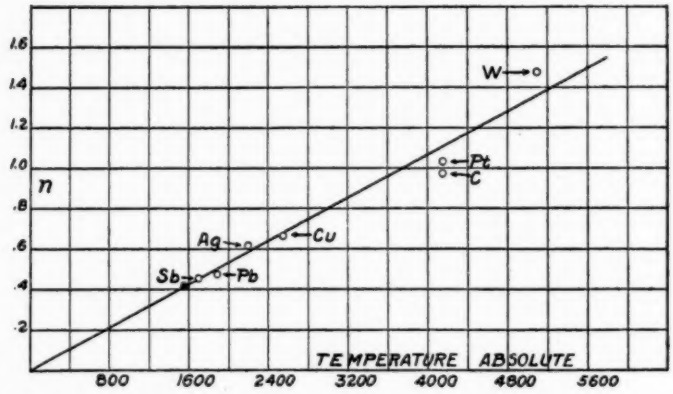

Fig. 7. Constant n of Nottingham's equation as a function of boiling temperature.

the metal. We have extended Nottingham's graph by two points, computing n for platinum from Ives curves[3] and n for tungsten from our own work. This is shown by Table II and Fig. 7.

TABLE II

Cathode	Anode	n	Authority	Boiling point	Authority
carbon	antimony	0.460	Nottingham	1710°K	Greenwood 1910
carbon	lead	0.480	"	1883	Van Liempt 1920
carbon	silver	0.624	"	2214	" " "
copper	copper	0.670	"	2562	" " "
copper	carbon	0.985	"	4187	" " "
platinum	platinum	1.15	Ives (Anderson)	4180	Langmuir 1914
tungsten	tungsten	1.487	Anderson & Kretchmar	5100	" "

The temperatures used were taken from Landolt-Bornstein Physikalischen-Chemische Tabellen, Fifth Edition, 1923 (except for platinum and tungsten) and are not quite the same as those given in Nottingham's paper. The questionable materials, aluminum, cadmium, and zinc are omitted from Table II and Fig. 6. Within the limits of experimental

[6] Steinmetz, Radiation, Light and Illumination, McGraw-Hill, New York, p. 140.

error the points fit a straight line. If more precise determinations verify the validity of Nottingham's equation and the linear relation of n to the absolute temperature of the boiling point of the anode, we shall have a new method of finding the boiling points of metals.

We wish to express our appreciation of the assistance given in this experimental work by the Bosch Magneto Corporation who furnished materials and by Mr. L. F. Curtis, Chief Engineer, who gave valuable advice and suggestions from his experience with ignition circuits. The oscillograph used was kindly loaned by the Department of Electrical Engineering, University of Washington.

DEPARTMENT OF PHYSICS,
UNIVERSITY OF WASHINGTON,
SEATTLE, WASHINGTON,
March 18, 1925.

THE IONIZATION OF HYDROGEN BY ELECTRON IMPACT AS INTERPRETED BY POSITIVE RAY ANALYSIS*

By T. R. Hogness and E. G. Lunn

Abstract

Ions produced in hydrogen by electron impact.—Using an apparatus previously described in which positive ions formed by impact of electrons of definite energy (V_1+V_2) are accelerated and then deflected magnetically around a semi-circle into a Faraday cylinder, the relative numbers of ions of types H^+, H_2^+ and H_3^+ were measured *as a function of pressure* from $<0.1\times10^{-4}$ mm to .006 mm, and also *as a function of impact energy* (V_1+V_2) to 60 volts. At low pressures only H_2^+ ions are formed; as the pressure is increased the percentage of H_3^+ increases in proportion to the pressure. In the apparatus used, the percentage of H^+ increased with pressure but did not exceed 4 percent, while the percentage of H_3^+ ions reached 60. These results confirm the conclusions of Dempster and Smyth that the primary process in the ionization of hydrogen is the ionization of the molecule without dissociation. The previously measured ionization potential at 16 volts (confirmed in this work) is that for the formation of H_2^+. H_3^+ also appears at this potential, but as a result of a secondary process. It appears that the H_2^+ ion is readily dissociated by collision and that the H^+ ion formed may unite with the H_2 molecule collided with or with some other molecule to form H_3^+. The interpretation of ionization potentials reported by other observers is discussed in the light of these results.

Ions produced in helium containing hydrogen, by electron impact.—The percentage of H^+ ions found was greater even than the percentage of H_2^+, while no H_3^+ ions were observed. Evidently the primary ions H_2^+ are readily dissociated by impact with He atoms. Evidence was found for the ions HeH^+ and also for an ion with $m/e=6$, perhaps HeH_2^+.

IN a recently published preliminary report[1] the authors have described the apparatus employed in this investigation and have given the conclusions that could be drawn from the scanty results then available. By changing the experimental procedure and widening the range of experimental conditions employed they have since made a more detailed study of the problem. The results of this study have made untenable the conclusion formerly drawn that in the ionization of hydrogen by electron impact there are two independent primary processes

$$H_2=H_2^++\epsilon \qquad (1)$$

$$H_2=H^++H+\epsilon \qquad (2)$$

* When this paper was first submitted the authors were informed by the editor that an article by H. D. Smyth, "Primary and Secondary Products of Ionization in Hydrogen," was already in press (Phys. Rev. **25**, 452, April 1925). Through the kindness of the editor we have had the advantage of reading proof of that article and have accordingly revised the discussion in this paper to give recognition to Smyth's work.

[1] Hogness and Lunn, Proc. Nat. Acad. Sci., **10**, 398 (1924).

and have given evidence that Eq. (1) represents the only primary process, the formation of H^+ and H_3^+ being secondary. This is the conclusion drawn by Dempster[2] in a much overlooked and neglected paper from his investigation of the ionization of hydrogen by high-voltage electrons, and also by Smyth.[3]

Description of the Apparatus and Method

The apparatus (Fig. 1) is essentially an ionization potential tube so arranged that the products of ionization can be analyzed by Dempster's[4] positive-ray method. The preliminary report of this work gives a detailed description of the apparatus which need not be repeated here. Consideration of the equation $e/m = 2V_4/H^2r^2$ by means of which

TABLE I

Electrometer readings for H^+, H_2^+ *and* H_3^+ *peaks, at various pressures.*

Pressure (10^{-4} mm)	Readings			Percent		
	H^+	H_2^+	H_3^+	H^+	H_2^+	H_3^+
<0.1	0	360	0	0	100	0
	0	241	0	0	100	0
2.0	5	520	1.3	0.9	96.7	2.4
	3	434	0.8	0.7	97.5	1.8
5.4	17	850	35	1.9	94.2	3.9
	17	630	33	2.5	92.6	4.9
	18	900	49	1.9	93.0	5.1
11	8	500	94	1.3	83.1	15.6
	5	320	45	1.3	86.5	12.2
12	7	520	103	1.1	82.6	16.3
	10	512	115	1.6	80.1	18.3
15	15	530	110	2.3	81.0	16.7
22	1(?)	220	69	0.3(?)	75.9	23.8
	33	1000	265	2.5	77.1	20.4
28	28	560	260	3.3	66.1	30.6
	27	560	240	3.3	67.7	29.0
39	61	720	540	4.6	54.5	40.9
	27	520	360	3.0	57.3	39.7
56	40	470	690	3.3	39.2	57.5
	36	460	680	3.1	39.1	57.8
He and H_2	153	70	0	68.6	31.4	0

[2] Dempster, Phil. Mag. **31,** 438 (1916).

[3] H. D. Smyth, Phys. Rev. **25,** 452 (April 1925). See also Proc. Roy. Soc. **102A,** 283 (1922); **104A,** 121 (1923); **105A,** 116 (1924); Nature, **111,** 810 (1923); **114,** 124 (1924); Phys. Rev. **23,** 297 (1924); J. Franklin Inst. **198,** 795 (1924).

[4] Dempster, Phys. Rev. **11,** 316 (1918).

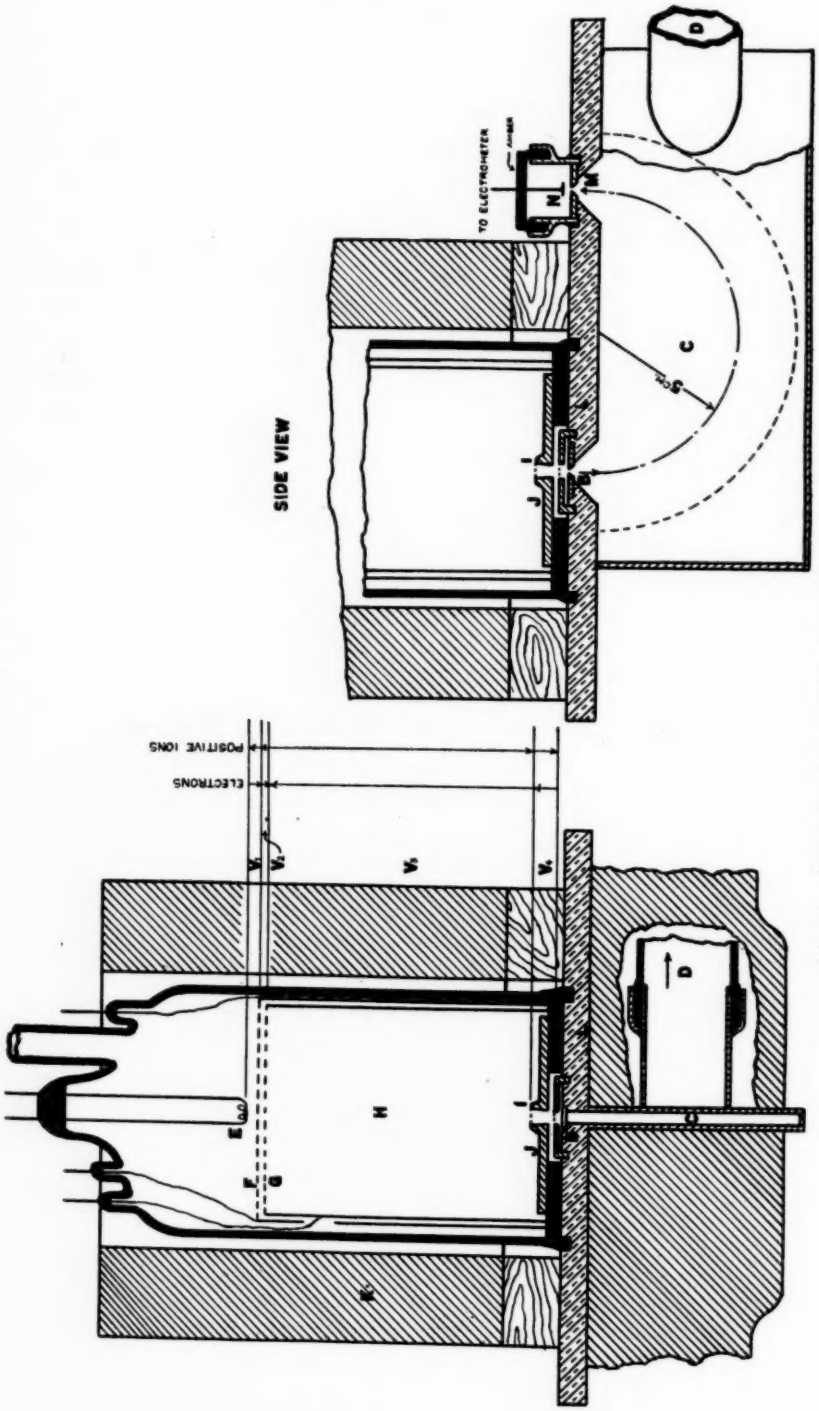

Fig. 1. Apparatus for positive ray analysis of ions.

the specific charges are determined, shows that two experimental procedures are open, (1) that of keeping the magnetic field H constant and focussing the ion beam by varying the accelerating potential V_4, and (2) that of varying the magnetic field while V_4 is kept constant. The former procedure was used in searching for new ions and for measuring their specific charges, the latter in measuring the ionic intensities since its use permitted constancy of electrical conditions in the tube and gave consistent and reproducible results.

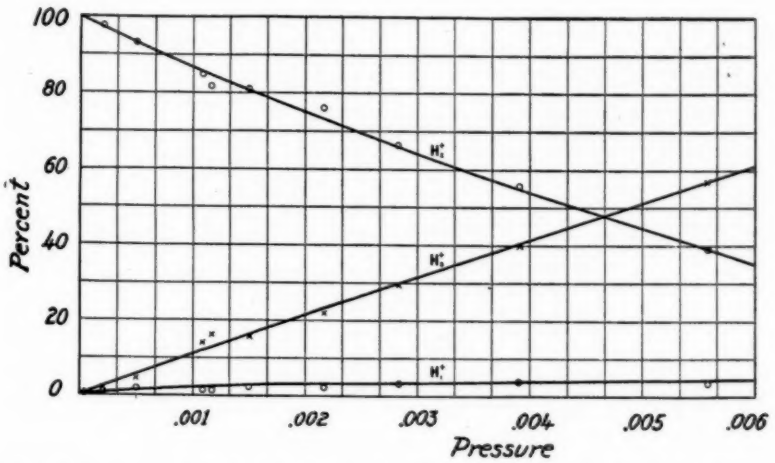

Fig. 2. Percentage of each of ionic species (H^+, H_2^+, H_3^+) as a function of pressure.

Of the present experiments those that seem to throw most light on the problem of interpreting the processes of ionization are the ones on the change of the relative intensities of the ions H^+, H_2^+ and H_3^+ with change in pressure. The data from these experiments are recorded in Table I. The electrometer deflections given were obtained with the constant deflection method. The right-hand side of Table I gives the percentage of each ionic species present as measured by the electrometer deflection ratio. The averages of the values for each pressure given in the table are plotted in Fig. 2, in which the pressures are recorded as abscissas and the percentages as ordinates.

It is evident from the table and from Fig. 2 that as the pressure is lowered the percentages of H^+ and H_3^+ decrease in a regular manner and approach zero at zero pressure. This clearly indicates that the formation of H_2^+ is the primary process and that H^+ and H_3^+ are formed from H_2^+ as the result of secondary collisions with gas molecules. H_2^+ is appar-

ently metastable and is disrupted when it collides with a neutral gas molecule in one of two ways

$$H_2^+ + H_2 = H_3^+ + H \tag{3}$$

$$H_2^+ = H^+ + H \tag{4}$$

If Eq. (4) represents the sole collision reaction then the formation of H_3^+ would be the result of the tertiary process

$$H^+ + H_2 = H_3^+ \tag{5}$$

Now if H_3^+ were formed only by the reaction (5), in order to account for the fact that the intensity of H^+ was very small at all pressures, it would be necessary to conclude that the proton has a much smaller mean free path than would be predicted from kinetic theory considerations. Hence it seems reasonable to suppose that when H_2^+ ions collide with neutral molecules the reaction taking place in the majority of cases is (3), and that reaction (4) takes place less often.

When the field V_3 for drawing the positive ions from the ionization chamber was increased to such an extent that only those electrons in the upper portion of that chamber had ionizing energy, then the intensity of $(H^+ + H_3^+)$ increased with respect to that of H_2^+ as might have been expected since the H_2^+ ions formed had greater chance of collision having had a longer average path to traverse. Moreover the ratio of the intensity of H^+ to that of H_3^+ increased considerably. This can be explained by assuming that under these conditions H_2^+ breaks up more often in accordance with reaction (4). This would happen if when the H_2^+ ion acquires sufficient energy before colliding, the H^+ formed by disruption were not trapped by the H_2 molecule to form H_3^+ but passed on into the resolving chamber.

There remains the possibility, however, that H_2^+ is stable and must acquire a definite velocity before a collision would result in disruption into H^+ and H. To examine this the change in the percentage of $(H_3^+ + H^+)$ with small variations of V_3 was studied. It was found that as V_3 was gradually lowered from 4.5 volts to 0.1 volt, $(V_1 + V_2)$ being 48 volts, the percentage of $(H_3^+ + H^+)$ increased very slightly instead of decreasing as might be expected if energy were required to cause H_2^+ to break up. Although inconclusive, this result seems to indicate that H_2^+ is energetically unstable. This conclusion is in accord with the following, deduced by Sommerfeld on theoretical grounds. "The H_2^+ ion is *unstable energetically*; it can dissociate into H and H^+, giving up energy. At the same time it follows from this for the ionization of the H_2 molecule that if this happens in the sense of scheme [Eq. (1)] it requires a greater

ionization potential than if it proceeds according to the scheme [Eq. (2)]. This conclusion is independent of any assumptions about the model of the neutral H_2, and also remains preserved if we pass from the H_2^+ molecule considered so far to a far more general molecule."[5]

In the experiments plotted in Fig. 2, 48 volts were applied to the impact electrons. The effects of slower speed electrons were investigated at one arbitrarily chosen pressure by obtaining the percentages of the several ions as a function of (V_1+V_2) (Fig. 3). The increase in the percentage of H_3^+ as (V_1+V_2) was decreased may be explained as due to the characteristics of the discharge tube. The now greater retarding potential V_3 decreased the velocity of those electrons that had penetrated into the lower part of the ionization chamber (H of Fig. 1) to such an extent that they could not ionize the gas. The H_2^+ ions were then formed at a greater average distance from the gauze I, and having had a longer

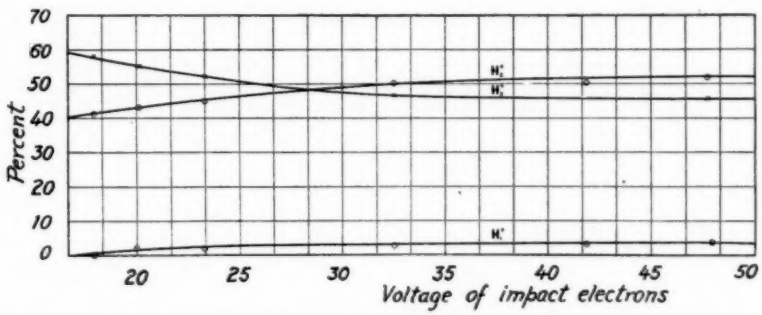

Fig. 3. Variation in relative numbers of H^+, H_2^+ and H_3^+ ions with energy of impact electrons.

average path to traverse had greater chance to collide. The curves of Fig. 3 could not be extended below 18 volts with accuracy because of the small intensity of each of the ionic species. Little significance, moreover, can be attached to the H^+ percentage curve at low voltages because of the inaccuracy of measurement of the small H^+ ion current in this region. From these observations of Fig. 3, we conclude that the processes described above are also true for impact electrons of smaller velocities.

Some experiments were made on relative ionic intensities in mixtures of helium with a relatively small amount of hydrogen. It was found that the percentage of H^+ was much greater than in pure hydrogen at any pressure employed (see the last line of Table I). Under these conditions the reactions designated by Eqs. (3) and (5) are much less probable and the H_2^+ on collision with the He atom disrupted to form H^+.

[5] Sommerfeld, "Atomic Structure and Spectral Lines," 1st Eng. Ed. Appendix 14, page 605.

With mixtures of helium and hydrogen in the tube two particularly interesting intensity peaks of $m/e=5$ and a less definite one at about $m/e=6$ were observed repeatedly. A typical run showing these is plotted in Fig. 4. Although the small amount of these ions did not permit of a study of their origin, there is little doubt that the $m/e=5$ ion is the ion of helium hydride, HeH^+, while the other may be HeH_2^+.

The Ionization Potential

To determine the ionization potential for the formation of H_2^+, V_4 was set to give the peak of the H_2^+ intensity curve and with the magnetic

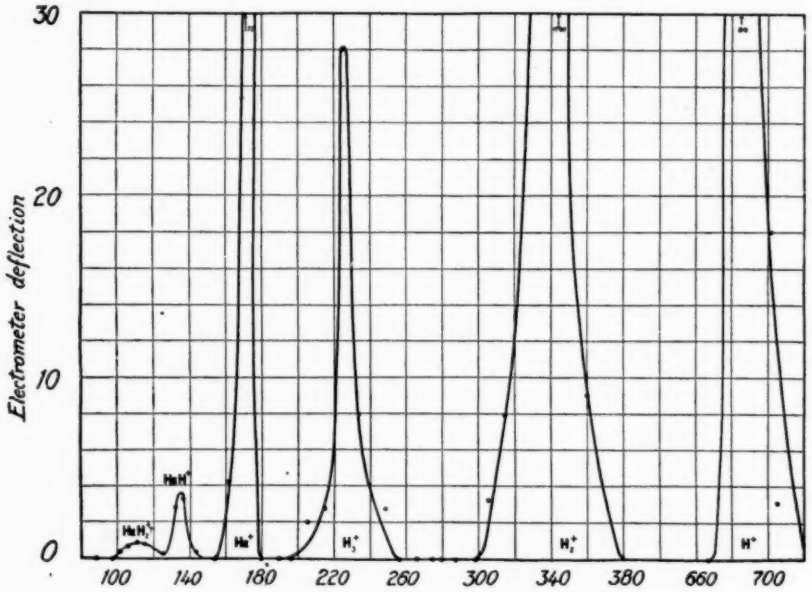

Fig. 4. Peaks obtained with mixture of He and H_2.

field, the filament current, V_1 and V_3 all held constant, the electrometer current was noted as V_2 was decreased in steps of 0.3 volt. When the rate of deflection of the electrometer was plotted against V_1+V_2, curves like that of Fig. 5 (labelled H_2^+) were obtained. The point at which each curve cut the zero ordinate was taken as the approximate (uncorrected) value of the ionization potential. Then by setting V_1 and V_2 immediately above and below this, and observing the electrometer deflection over a long period of time, a more accurate value was obtained.

To obtain the necessary correction to be applied because of the initial velocity of the electrons, the potential drop along the filament, and contact differences of potential, and to take into account the sensitivity of

the apparatus, helium was introduced into the tube and the ionization potential curve for He^+ obtained in a manner analogous to that described for H_2^+. (See Fig. 5, He^+.) 24.5 volts was taken as its true ionization potential. In order that the corrections thus found should have any significance it was necessary to choose the hydrogen and helium pressures such that (1) the "saturation" intensities of He^+ and H_2^+ be the same, and (2) the ionization potential curves for helium and for hydrogen be of approximately the same shape. This choice of pressures was made as follows. It was found that 50-60 volts was above the "saturation" voltage. The intensity of the He^+ line in the calibration run when V_1+V_2 was about 60 volts was therefore noted, the helium then pumped out, and hydrogen introduced at such a pressure as gave a H_2^+ line of this same intensity. The smaller figure of Fig. 5 shows the appearance of the ionization potential curves for the He^+ and H_2^+ when the respective pressures were so chosen. The two curves are evidently almost superposable.

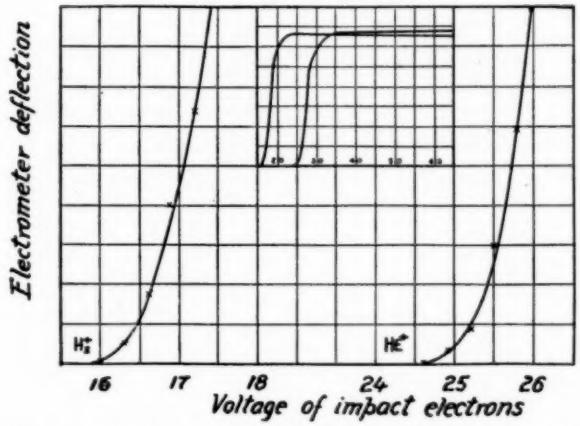

Fig. 5. Variation of intensity of peaks H_2^+ and He^+ with energy of impact electrons.

The corrected values for the ionization potential of hydrogen found in successive runs are: 16.3, 16.5, 15.7, 15.8, 16.1, 15.9, 15.8, 15.8. The average value is 16.0.

To show that H_3^+ and H_2^+ appear at the same ionization potential, the pressure was so regulated that the H_3^+ and H_2^+ lines were of equal intensity and the potentials for the formation of the two ions compared. Under these conditions the two potentials were identical, but at lower pressures where H_2^+ predominated, H_3^+ and H^+ were not detected at as low voltages as was H_2^+.

The several lines of investigation presented above unite then in giving evidence that, in the ionization of hydrogen by electron impact, the

primary process of ionization is the detachment of an electron from a molecule ($H_2 = H_2^+ + \epsilon$) and that the H_2^+ thus formed is probably energetically unstable and can break up on collision to give H^+ (and H). The evidence that the formation of H^+ is the result of a secondary process may be briefly summarized. (1) At very low pressures no H^+ was found; (2) H^+ was never found with impact electrons having a velocity lower than the minimum necessary for the production of H_2^+; and (3) with mixtures of helium and hydrogen large amounts of H^+ were found.

The following then are the conditions for producing in a discharge tube each of the different ions of hydrogen in predominating amounts: For H^+, large potential difference and the addition of some inert gas such as helium; for H_2^+, low pressures; for H_3^+, higher pressure and small potential difference.

Discussion

It is of interest to note that the above results and the main conclusions derived therefrom are exactly in accord with the following conclusion of Dempster[2] who used 800 volt electrons in his experiments: ". . . . electrons ionize only by detaching a single electron from the molecule, and are not able to dissociate the molecule into atoms." Graphical analysis of his intensity ratios shows also that at zero (extrapolated) pressure no H^+ or H_3^+ would be formed. The present conclusions also agree in the main with those of Smyth,[3] differing therefrom only in detail as to the secondary process. He concludes that the formation of H_3^+ is a tertiary process while we believe it to be largely a secondary one (Eq. 3). Smyth's Fig. 6 shows in a striking manner the increase of H_3^+/H^+ with decrease of V_3. This we believe gives support to our view. In discussing the stability of H_2^+, Smyth maintains that if that ion were stable with respect to H^+ and H, the additional energy necessary for its disruption would have to be supplied by the impacting electron; but this energy could also be supplied by the kinetic energy of the H_2^+ acquired from the electrical field. The possibility may be pointed out here that, contrary to the conclusions drawn from theoretical considerations, H_2^+ may be stable with respect to H^+ and H, and yet be unstable with respect to H_3^+, i.e. the reaction (3) may take place with evolution of energy while that of equation (5) may not. There does not seem to be as yet sufficient experimental evidence to test this possibility.

The recently reported spectroscopic investigations of Richardson and Tanaka[6] on low voltage arcs in hydrogen lead them also to conclude that the primary process of ionization is the formation of H_2^+.

[1] Richardson and Tanaka, Proc. Roy. Soc. **106A**, 663 (1924).

It may be well to discuss the bearing of the results of the positive ray studies on critical potential measurements. Table II gives the measurements of several observers on the critical potentials which they

TABLE II

Ionization potentials of hydrogen.

Observers	Values in volts				
Davis and Goucher[7]	11		15.8		
Bishop[8]	11		15.7		
Found[9]			15.8		
Compton and Olmstead[10]	10.8		15.9		
Krüger[11]	11.5		16.4		29.7
Boucher[12]		13.6	15.6		
Foote and Mohler[13]			16.0		
Mohler, Foote and Kurth[14]			16.0		
Olmstead[15]	11.5	13.6	16.0		
Horton and Davies[16]		13.5	15.9	22.8	29.4
Mackay[17]			15.8		
Olson and Glockler[18]			16.7		
Olmstead and Compton[19] (2800°C)		13.5			
Smyth[3]			16.0		
	Mean		16.0		

ascribe to ionization of hydrogen. All are in agreement concerning the existence of an ionization potential at about 16 volts, but all except Smyth have interpreted this potential as that at which ionization plus dissociation (Eq. 2) takes place. This interpretation is obviously no longer tenable. The 13.5 volt point observed has been ascribed to ionization of the hydrogen atom, the atomic hydrogen presumably being formed by thermal dissociation or by collision of an excited hydrogen molecule with an unexcited one (see below). The potential at about 11 volts which has been interpreted by some observers as that for the process $H_2 = H_2^+ + \epsilon$, is probably due to excitation, or, as suggested by Horton and Davies,[20] to the ionization of mercury vapor. A new interpretation must

[7] Davis and Goucher, Phys. Rev. **10**, 101 (1917).
[8] Bishop, Phys. Rev. **10**, 244 (1917).
[9] Found, Phys. Rev. **16**, 41 (1920).
[10] Compton and Olmstead, Phys. Rev. **17**, 45 (1921).
[11] Krüger, Ann. der Phys. **64**, 288 (1921).
[12] Boucher, Phys. Rev. **19**, 189 (1922).
[13] Foote and Mohler, Origin of Spectra, p. 68.
[14] Mohler, Foote and Kurth, Phys. Rev. **19**, 414 (1922).
[15] Olmstead, Phys. Rev. **20**, 613 (1922).
[16] Horton and Davies, Phil. Mag. **46**, 872 (1923).
[17] Mackay, Phil. Mag. **46**, 828 (1923); Phys. Rev. **24**, 319 (1924).
[18] Olson and Glockler, Proc. Nat. Acad. Sci. **9**, 122 (1923).
[19] Olmstead and Compton, Phys. Rev. **22**, 559 (1923).
[20] Horton and Davies, loc. cit.[16] In their helium studies they were able to detect mercury vapor spectroscopically in spite of precautions taken to prevent its entrance.

also be sought for the 22.8 volts potential of Horton and Davies, and for the 29.4 and 29.7 points of these observers and of Krüger respectively. The first was ascribed to molecular ionization, the second to molecular dissociation with ionization of both atoms, $H_2 = 2\,H^+ + 2\epsilon$. If such a process as this last took place the lower curve of Fig. 3 would show an increase in the percentage of H^+ at about 30 volts. Olson and Glockler[18] found nine critical potentials in the interval between 14.86 and 16.68 volts, five of which, in addition to the ionization potential, are each 3.16 volts greater than a resonance potential or ionization potential of atomic hydrogen. They interpret these five critical potentials as measuring the energy necessary to dissociate the molecule and resonate one of its atoms, the 3.16 volts being then the heat of dissociation. The three remaining lines which have no apparent relation to the Lyman series they ascribe to molecular excitation not accompanied by dissociation. Hughes[21] in considering Smyth's earlier work in the light of his own experiments, concluded that excitation by electron impact is often accompanied by dissociation. If this view is accepted the interpretation of Olson and Glockler's work, with the exception of the ionization potential, remains unchanged. Von Keussler,[22] however, concluded from a study of spectral data, including his own, that dissociation is an effect secondary to molecular excitation and occurs if the excited molecule is disturbed, as by collision, before it has time to radiate. Such dissociation by collision results only if the excited molecule has energy in excess of that necessary to dissociate the molecule and produce the excited atom. In view of the present experiments and those of Smyth, it appears that von Keussler's theory is the more logical one. There can be very little difference between an ionized molecule and one in the higher stages of excitation. If dissociation does not accompany ionization it would hardly be expected to accompany excitation. If von Keussler's view is adopted, the interpretation of Olson and Glockler's work follows immediately. The 3.16 volts represents, then, the energy of the excited molecule in excess of the energy of the excited atom. If the excited molecule is energetically unstable with respect to its dissociation products and radiates energy or produces kinetic energy on dissociation, the heat of dissociation must then be less than 3.16 volts. While this excess energy of the excited molecule may not be the same for all stages of excitation, any differences that exist may be small enough to fall within the limits of error of the measurements of Olson and Glockler.

[21] Hughes, Phil. Mag. **48**, 56 (1924).
[22] Von Keussler, Zeits. f. Physik, **14**, 19 (1923).

It may be of interest to note that the results of the experiments on mixtures of helium and hydrogen described above point toward an explanation of Merton and Nicholson's[23] experiments on the extension of the Balmer series in which they observed more lines of this series in mixtures of helium with relatively small amounts of hydrogen than could be detected in pure hydrogen.

Taking the mean of the experimental data recorded in Table II gives 16.0 volts as the ionization potential of hydrogen for the formation of H_2^+. As the H_2^+ ion is probably unstable with respect to H and H^+, it must give off energy when it dissociates. If ionization could take place according to the scheme in Eq. (2) the ionization potential for such a process would then be less than 16.0 volts, assuming this to be the correct value, and the heat of dissociation would then be less than $16.0-13.5=2.5$ volts, equivalent to 57,500 calories per mol. Langmuir,[24] Isnardi,[25] and Wohl,[26] by indirect methods obtained 84,000, 95,000 and 90,000 calories per mol respectively for this value. In view of the probable uncertainty of the values obtained by both these lines of investigation, we are not yet ready to assume that this discrepancy is a real one.

The several theoretical models for H_2^+ give values for the ionization potential of H_2 higher than the observed 16.0 volts. The Bohr model, considered untenable for other reasons, leads to the value 17.85 volts (2.20 Rh − 0.88 Rh), the Pauli[27] model to 23.7 volts, and the various models of Niessen[28] to values 23.5 to 28.8 volts.

DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA,
February 9, 1925.

[23] Merton and Nicholson, Proc. Roy. Soc. **96A**, 112 (1919).
[24] Langmuir, J. Am. Chem. Soc. **34**, 860 (1912); Langmuir and Mackay, ibid. **36**, 1708 (1914); Langmuir, ibid. **37**, 417 (1915).
[25] Isnardi, Zeits. Elektrochem. **21**, 404 (1915).
[26] Wohl, Zeits. Elektrochem. **30**, 49 (1924).
[27] Pauli, Ann. der Physik **68**, 117 (1922).
[28] Niessen, Physica **2**, 345 (1922); Ann. der Physik **70**, 129 (1923).

CRYSTAL STRUCTURE OF TITANIUM AND CHROMIUM*

By R. A. Patterson

Abstract

Precision measurements of the crystal structure of these two metals in very pure form have been made. For chromium (99.8 percent) a body-centered cubic structure, with $a_0=2.872$A, is found; for titanium (99.9 percent) an hexagonal close-packed structure, with $a_0=2.951$A; axial ratio $c=1.590$. These structures are of the type previously assigned by A. W. Hull, but differ slightly in numerical values. They were measured in comparison with copper using Davey's value of $a_0=3.597$A for pure copper. The *densities* computed from these results come out 4.49 for Ti and 7.23 for Cr. Heat treatment had no effect on the crystal form for Ti, merely changing the size of the crystals.

Specimens

THE crystal structures of titanium and chromium have been determined using samples of pure metals. These samples were provided by M. A. Hunter who reduced the metals from pure chlorides with sodium.[1] The temperature of the reaction was sufficiently high to result in fusion—the metals coming out when cold in the form of pellets. These pellets were ground, washed, and then sprinkled in shellac on narrow ribbons of paper or cardboard. These ribbons constituted the specimens analyzed.

Method

The standard x-ray diffraction apparatus developed by Hull and Davey was employed. It has been fully described in their papers.[2,3] The diffraction pattern due to chromium was accompanied on each spectrogram, for calibration purposes, by that due to copper. Each diffraction image is double, being produced by the α_1 and α_2 lines in the K spectrum of molybdenum, which have wave-lengths of 0.7078 and 0.7121A, respectively. It is possible by the application of a properly constructed scale to read off for each diffraction image the spacing of the set of planes giving rise to it, divided by the order of interference. This was done for each image produced by the α_2 radiation. The structure of copper is face-centered cubic and has been accurately measured by Davey.[4] Using his

* The results of this paper were presented before the American Physical Society at the New York Meeting, February 28, 1925 (Phys. Rev. **25**, 581, 1925).

[1] M. A. Hunter, J. Am. Chem. Soc. **32**, 330 (1910).

[2] A. W. Hull, Phys. Rev. **10**, 661 (1917).

[3] W. P. Davey, J. Opt. Soc. Am. **5**, 479 (1921).

[4] W. P. Davey, Phys. Rev. **25**, 753 (June 1925).

value of $a_0 = 3.597$A, corrections due to any irregularities in the film were easily made. It was not necessary to locate the zero line on the film with the known diffraction pattern of copper present.

In the spectrograms of titanium, usually the two Kα lines of molybdenum were not resolved as they were in the case of chromium and copper. Consequently the centers of the diffraction images were read, and a negative correction of 0.25 percent was applied to each reading in order to obtain the value for the α_2 radiation.

The use of copper instead of rock salt for a comparison pattern is recommended to those using this type of equipment for the following reasons. First, narrow flat wires can easily be made; second, these will give well defined diffraction images in which both α lines are resolved throughout the length of the film; third, Davey has completed accurate measurements of the parameter for copper in terms of rock salt and has shown that the usual impurities in ordinary conductivity copper do not appreciably affect its lattice parameter.

DATA

Tables I and II contain the observed data for titanium and chromium respectively. In the first column are given the indices of the planes giving rise to each diffraction image. The numbers in the second column

TABLE I

Results for titanium. Close-packed hexagonal structure.
Sample used was 99.9 percent pure.

Planes	Intensity	Plane spacing/order Film 1	Film 2	Film 3	Film 4
10.0	4	2.556A	(2.540)A	2.551A	(2.544)A
00.1(2)	4	2.341	2.346	2.341	(2.335)
10.1	10	2.241	2.244	2.241	2.235
10.2	4	1.728	1.731	1.724	1.727
11.0	4	1.477	1.477	1.474	1.472
10.3	5	1.336	1.339	1.332	1.337
11.2	4	1.249	1.250	1.247	1.251
20.1	3	1.233	1.236	1.235	1.235
00.1(4)	1	1.176	1.176	1.173	(1.178)
10.1(2)	1	1.125	1.125	1.124	(1.121)
10.4	2	1.065	1.071	1.066	(1.069)
20.3	3	.989	.991	.989	.991
12.1	3	.942	.947	.945	.948
11.4	3	.917	.917	.918	.9185
10.5	1	.880	.884	.882	.881
10.2(2)	0	.849			
12.3	0	.8195	.820	.823	.822
30.2	0	.800			
	Mean a_0 =	2.951A	2.954A	2.947A	2.951A

Average $a_0 = 2.951$A

Corresponding density = 4.49 gm/cc; density by Hunter and by Mixter = 4.50 gm/cc.

specifying intensity are arbitrary, indicating relative order of intensities, but not ratios of intensities. To save space the average numbers for the films measured are given. The corrected plane spacings divided by the order of interference are recorded in the remaining columns. Each column represents a separate film and specimen. The application of a factor, computed from the geometry of the structure, to each plane spacing gives a_0, the side of the unit cell. At the foot of each column of plane

TABLE II

Results for chromium. Body-centered cubic structure.
Sample used was 99.8 percent pure.

Planes	Intensity	Plane spacing/order Film 1	Film 2	Film 3
110	10	(2.052)A	(2.044)A	(2.037)A
100	4	1.436	1.435	1.436
211	8	1.172	1.174	1.173
110(2)	5	1.014	1.015	1.017
310	6	.909	.908	.909
111	2	.829	.830	.830
321	7	.768	.768	.769
100(2)	1	.718		.719
411, 110(3)	4	.6775	.6770	.6778
210	3	.6420	.6416	.6432
332	3	.6120	.6121	.6130
211(2)	3	.5865		.5870
431,510	4	.5630	.5645	.5632
	Mean a_0=	2.871A	2.873A	2.873A

Average a_0=2.872A

Corresponding density=7.23 gm/cc; density by Moissan=6.92 gm/cc.

spacings is given the average value of a_0 as computed from that film. Only those values of the spacings that were obtained from clear cut diffraction images were used in the determination of the lattice parameters. The others are placed in parentheses.

RESULTS

Titanium. The relative position of the diffraction images and their relative intensities indicate clearly the close-packed hexagonal structure for titanium, as previously found by Hull.[5] The axial ratio was determined by the graphical method of Hull and Davey,[6] to be $1.590 \pm .002$. The density from these measurements comes out 4.49, whereas Hunter and also Mixter obtained 4.50 gm per cc.

The diffuseness of the diffraction images and their lack of resolution are ascribed to the minuteness of the individual crystal grains—not to the powder grains.

[5] A. W. Hull, Science **52**, 227 (1920); Phys. Rev. **18**, 88 (1921).
[6] Hull and Davey, Phys. Rev. **17**, 549 (1921).

Different specimens were subjected to different heat treatments in an endeavor to detect the existence of any other crystal structure between 0°C and 800°C. The four specimens that furnished the data in Table I were treated as follows:

Film 1: titanium had been dipped in liquid air.
Film 2: titanium had been heated to 850°C and quenched.
Film 3: titanium had been cooled 2½ hours in liquid air.
Film 4: titanium had been annealed at 850°C and cooled slowly.

No trace of polymorphism was found on any of these films. Some lines on Film 4 are resolved, indicating that long annealing at higher temperatures would permit further grain growth and higher resolution to be obtained.

Chromium. The diffraction patterns confirm the body-centered cubic structure for chromium previously found by Hull.[7] Sharp resolution and fair intensity extend across the film (through glancing angle of 45°) indicating that the crystal grains are sufficiently large to give higher orders of interference and good resolution, but not coarse enough to produce striated images. The computed density is 7.23 gm/cc, whereas Moissan gives 6.92 gm/cc.

The author wishes to express his thanks to Dr. M. A. Hunter for the pure metals and for many helpful suggestions, also his appreciation of the assistance rendered by Mr. W. C. Ellis and Mr. H. M. Faigenbaum in preparing specimens and in measuring films.

RENSSELAER POLYTECHNIC INSTITUTE,
March 15, 1925.

[7] A. W. Hull, Phys. Rev. **17**, 571 (1921).

PRECISION X-RAY MEASUREMENTS BY THE POWDER METHOD[1]

By F. C. Blake

Abstract

Corrections to x-ray spectograms obtained by the powder method.—Spectrograms were obtained with a semi-cylindrical camera of radius 16.65 cm giving lines on both sides of the undeflected beam, using a powder sample about 0.2 mm in radius held in an accurately centered hole. *Correction for film shrinkage* was made by using Al as a comparison. *Correction for penetration into the sample.* This is taken to cause a shift of each line δl equal to $d \cot \theta$, and a value of d is chosen so as to make the lattice constant a_c computed from the various lines, approximately the same, or if the constant is assumed known, as in the case of Al, to make the computed radius come out constant. In one test with Fe, the greatest variation from the mean a_c was only .1 percent, taking d as .006 cm. With samples of varying radius r, the value of d was found to vary from $+.006$ cm ($r = .15$ mm) to $-.014$ ($r = .72$ mm). Hadding's method of correction is discussed. It is suggested that a combination of the two methods, taking $\delta l = K_1 \theta \cot + K_2 r$, would give even more accurate results.

Lattice constant for pure iron is found to be $2.8603 \pm .0002$A.

THIS paper is an attempt to carry the precision methods reported by Havighurst, Mack and Blake[2] one step further. These authors found it possible in large measure to avoid serious error in their crystal structure measurements by calibrating their films by means of some known standard, the standard being intimately mixed with the sample to be investigated.

This method of calibration proved to be thoroughly reliable but a comparison of the results obtained by these investigators with those of this paper shows the advantage to lie with the method here described. Phebus and Blake found the method of intimate mixing of standard and unknown substance unworkable in the case of alloys; therefore, another had to be found.

Description of Apparatus

A water cooled x-ray tube with molybdenum target was surrounded with a cylindrical lead box somewhat after the manner of other experimenters.[3] A row of horizontal slits in the lead box allowed the free passage

[1] Presented before the American Physical Society as part of a paper by Phebus and Blake, Nov. 29, 1924 (Phys. Rev. **25,** 107, 1925).

[2] Havighurst, Mack and Blake, J. Amer. Chem. Soc. **46,** 2368 (1924).

[3] E. g. Davey, Gen. Elec. Rev. p. 565 (1922); also Bain, Chem. and Met. Eng. **25,** 657 (1921).

of x-rays from the target. A second set of slits placed just in front of the sample under investigation prevented secondary rays from entering the cameras. The cameras differed from the cassette system of Davey only in two important respects. First, each camera had a septum down its middle to separate the lines for the standard from those for the unknown under investigation, the sample tube being filled with the powder of the standard at one end and with that of the unknown at the other. The sample tube itself was like those used by Havighurst, Mack and Blake.[2] Second, the cameras were semi-cylindrical in form, thus permitting a complete set of lines on both sides of the undeflected beam. The cameras had a radius of 16.65 cm. They were very carefully machined throughout, the usual sheet aluminum being on the outside of each camera and the photographic film being held tightly against this by elastic webbing. The hole for holding the sample under investigation was first bored and then the walls of the camera were turned true in the lathe. This insured that each sample was accurately at the center of the photographic film.

The double displacements between corresponding lines were determined by means of a specially built comparator reading to 0.02 mm. Thus, except for errors of judgment in estimating the centers of lines, the displacement of a line from the zero was measured for aluminum to within 1 part in 5,000 for the nearest line and 1 part in 18,000 for the line farthest removed from the main central beam.

Sources of Error

The two chief sources of error which must be eliminated or corrected for in precision work are (1) the unequal shrinking of the photographic films, along with the influence of humidity upon their length and (2) the influence of the substance of the sample upon the absorption of the x-rays and consequently upon the registering of the rays upon the film. The first source of error is corrected for by calibrating the film by means of the standard whose space lattice is known, provided the inequality of absorption of the rays in the standard and in the unknown can be corrected for. If the proper correction for penetration can be found it must make the lattice dimensions independent of the glancing angle and independent of the diameter of the specimen under investigation. As will be seen this has been done.

Correction for Penetration into the Sample

In the precision work of Blake and Duane[4] in determining the value of the quantum of action by means of x-rays it was found that the penetra-

[4] Blake and Duane, Phys. Rev. **10**, 624 (1917).
[5] Blake, Proc. Nat. Acad. Sci. **4**, 237 (1918).

tion of the rays into the crystal introduced a serious error into the measurements unless it was obviated. This was done by having over the axis of the spectrometer not the front face of the crystal but the "effective plane" of the crystal. The effective plane was defined by them as that plane in the crystal at which if all the rays were diffracted into the ionization chamber, the ionization current would be the same as that due to the sum of all the diffractions at the various planes of the crystal. The writer[5] at the time derived theoretically an expression for the depth of the effective plane below the surface of the crystal that agreed entirely with the value found experimentally by Blake and Duane in the case of calcite. The correction formula for penetration into the sample used in this paper is based on similar ideas.

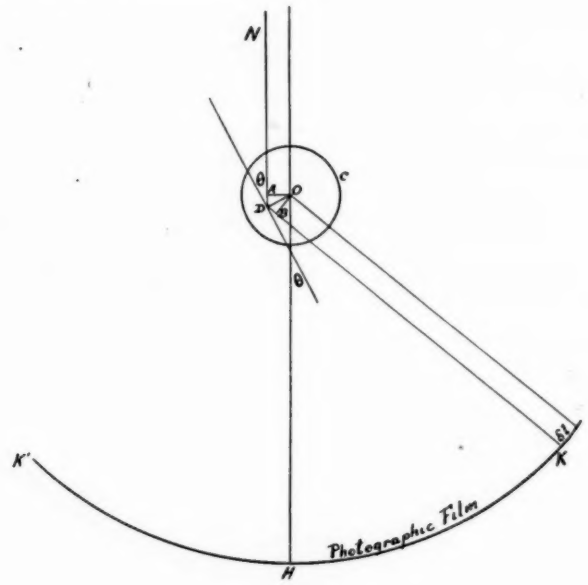

Fig. 1

In Fig. 1, O is the center of the sample under investigation, OC being the radius; O is also the center of the photographic film. Let AD be the distance of the effective plane below or above the center O. The central ray of the x-ray beam passes along OH. If H is the center of the undeflected beam and K is the position of the center of some line on the film, then $HK = \frac{1}{2}KK'$ where K' is the position of the mate of the line on the other side of the undeflected beam, assumed to be the same distance from H. Now the effective plane is defined as the plane from which the center of the line at K is reflected.

Then if OA and OB are normal to the incident and reflected rays respectively, we have $OA = OB = d \cot \theta$ where θ is the glancing angle and $d = AD$. Obviously, all lines on the film in order to give the same space lattice must be referred to the center O. Putting $HK = l$, if the so-called radius OH of the camera is large compared to d, $OB = \delta l$ very approximately, where δl is the correction to be applied to half the measured distance on the film between corresponding lines.

By inserting a zirconium oxide filter into each camera the x-rays are rendered monochromatic, only the $K\alpha$ doublet of molybdenum appearing on the film. In view of this fact, it seems probable that d should be the same for all the lines on the film, for so far as registering is concerned the average depth of penetration into the sample is certainly independent of the orientation of the minute crystals in the sample. If this is so then δl is proportional to cot θ. It would appear at once that the correction factor d cot θ would become absurdly large for very small values of θ, but it will be shown at the end of this paper that the true correction factor for substances easily penetrated by x-rays is K cot θ $\delta\theta$ where $\delta\theta$ is the angular width of each line; and while $\delta\theta$ is roughly constant for the different lines it does decrease with θ and thus prevents the correction becoming inordinately large for small angles. Experiments are now under way to test this with crystals having large space lattices in one direction at least. For those crystals studied to date, however, the error introduced in taking d constant instead of taking it proportional to the angular width of the lines is just barely outside the limit of experimental error of measurement.

Test of the Correction Factor for Penetration

A test of the correctness of the formula for δl can be seen illustrated in Table I. Aluminum was used as a standard to determine the space lattice of iron, aluminum itself having been previously found to have a space lattice constant of 4.0438 ± 0.0002A, by checking against very pure sodium chloride. The aluminum was "Baker analyzed," containing 0.02 percent SiO_2 and 0.01 percent Fe. In the light of the evidence submitted by Havighurst, Mack and Blake[2] on the effect of impurity upon space lattice it is clear that both the salt and the aluminum were effectively pure. The density of the aluminum used was 2.7068, this determination being made with a set of weights certified by the Bureau of Standards, conductivity water being used and buoyancy correction applied. Error due to surface tension of the suspending wire was eliminated. The calculated density was found to be 2.7104 using Richards'

value for the atomic weight of aluminum and Millikan's value for the mass of the hydrogen atom, viz., 26.96 and 1.662×10^{-24} gm. From the measured density the space lattice is computed to be 4.0456, which differs from the measured value by 0.045 percent, the accuracy being of course greater than that to which the mass of the hydrogen atom is known.

Table I gives for aluminum the measured displacement l, which as in all the tables is half of the double displacement, and l_c the corrected value of l where $l_c=l+d_1\cot\theta$. By trial d_1 was chosen so as to make the camera radius r_c constant, r_c being equal to $l_c/2\theta$ where θ satisfies Bragg's well-known equation. The uncorrected radius r computed from the values of l is also given. The greatest percent of variation from the mean value of r_c is 0.09.

TABLE I

Results for aluminum and iron

Diameter of samples 0.378 mm; d taken as .005 cm for Al and .006 cm for Fe.

Aluminum					Iron				
Face	l (cm)	l_c (cm)	r (cm)	r_c (cm)	Face	l (cm)	l_c (cm)	a (cm)	a_c (cm)
111	5.072	5.105	16.612	16.722	110	5.869	5.903	2.8763	2.8598
200	5.873	5.901	16.638	16.718	200	8.374	8.397	2.8661	2.8584
220	8.377	8.397	16.691	16.732	211	10.325	10.344	2.8626	2.8574
311	9.876	9.892	16.713	16.741	220	12.008	12.024	2.8582	2.8546
222	10.326	10.342	16.708	16.735	310	13.498	13.512	2.8591	2.8564
400	11.990	12.003	16.708	16.726	222	16.164	16.176	2.8590	2.8570
331	13.123	13.135	16.709	16.725	411 } 330 }	18.554	18.564	2.8600	2.8587
420	13.487	13.498	16.714	16.728					
422	14.867	14.871	16.714	16.725					
333	15.838	15.848	16.715	16.728					
440	17.374	17.383	16.716	16.725					
531	18.255	18.263	16.714	16.721					
442	18.542	18.550	16.712	16.718					
			Mean	16.726				Mean	2.8575

Using the mean corrected camera radius one can determine the space lattice for iron, a uncorrected and a_c corrected. Here the iron lines were corrected by an amount $\delta l=d_2\cot\theta$ where d_2 was found by trial to be 0.006 cm. Just as column 5 is a great improvement over column 4 so is column 10 a great improvement over column 9, the greatest percent of variation from the mean value of a_c being 0.10.

Of course it does not yet appear that there may not be some systematic error in all of the results of Table I, a table which is typical of the degree of reproducibility of the results both of this paper and of the paper of Phebus and Blake.

PENETRATION CORRECTION FACTOR AS A FUNCTION OF SAMPLE DIAMETER

To reduce the chance of a systematic error in the measurements it was thought worth while to investigate the influence of sample diameter upon

the penetration and to determine its correction factor. The diameter of the sample was varied from 0.25 mm to 1.45 mm by steps, using aluminum as a standard and iron as unknown, great care being taken in each case to have the sample properly centered in the camera. Table II gives the results for iron uncorrected for penetration, the camera radius as de-

TABLE II

Results for iron uncorrected for penetration.

Diam. of sample	r_c	Edge of iron cube in angstroms for various faces 110	200	211	220	310	222	321	Mean
0.276mm	16.592cm	2.8694	2.8658	2.8606	2.8589	2.8572	2.8572	2.8570	2.8609
0.378	16.726	2.8763	2.8661	2.8626	2.8582	2.8591	2.8590	.....	2.8635
0.586	16.724	2.8564	2.8569	2.8565	2.8588	2.8591	2.8584	2.8571	2.8576
0.798	16.604	2.8404	2.8538	2.8532	2.8528	2.8540	2.8527	2.8525	2.8514
1.045	16.585	2.8382	2.8456	2.8469	2.8483	2.8524	2.8487	2.8530	2.8476
1.442	16.726	2.8166	2.8316	2.8352	2.8392	2.8381	2.8406	2.8466	2.8354

termined by aluminum being corrected, however, in the manner indicated above. This table shows very plainly the need for a proper correction for penetration.

When this correction is applied the results obtained are as indicated in Table III. It will be noticed that the true space lattice for iron is here shown to be entirely independent of sample diameter for samples less than 1 mm in diameter.

TABLE III

Results for iron corrected for penetration.

Sample diam. (mm)	d_1 (Al) (cm)	d_2 (Fe) (cm)	r_c (cm)	Edge of iron cube in angstroms Deviation from each mean in angstroms $\times 10^4$ 110	200	211	220	310	222	321	Mean
0.259	.003	.006	16.658	+ 7	+ 5	− 5′	− 6	−10	.....	− 1	2.8570
0.276	.003	.004	16.592	− 2	+17	−19	−25	−11	+12	+ 2	2.8575
0.378	.005	.006	16.726	+26	+13	+ 2	−26	− 8	....	− 2	2.8572
0.502	.006	.004	16.713	− 4	− 1	− 2	+16	+12	+ 2	−25	2.8571
0.586	.006	.000	16.724	−12	− 6	−11	+12	+15	+ 8	− 5	2.8576
0.593	.004	−.001	16.605	+22	+10	− 7	−31	−16	−10	0	2.8579
0.678	.003	−.004	16.595	0	+12	−28	− 9	− 3	+20	+ 3	2.8576
0.798	.003	−.0055	16.604	+ 6	+45	+ 8	−30	− 3	−21	−14	2.8575
0.798	.003	−.004	16.592	+ 1	+23	+ 2	−22	+ 8	−19	+ 5	2.8582
1.045	.004	−.007	16.585	(+28)	(+ 6)	(−13)	(−17)	(+14)	(−28)	(+ 8)	(2.8543)
1.442	.004	−.014	16.726	(+47)	(−32)	(−13)	(−16)	(+27)	....	(−13)	(2.8501)
				Final mean 2.8575 ± .0002A							

Plotting the depth of the effective plane d against the diameter of the sample gives the curves of Fig. 2, the values for Al being indicated by crosses, those for Fe by circles. The curve for aluminum is seen to be a horizontal straight line, that for iron to be a straight line having a large

slope. No attempt was made to determine d closer than to within 0.0005 cm, for the final individual results of Table III have the actual errors of measurements on the double displacement still in them.

Since one has no good check on the density of the powder in the sample tube it is not surprising that both for aluminum and for iron the penetration correction factor has points apparently badly off the curve. Obviously, an accurately linear relation could only be expected if all samples had the same density of packing in the sample tube.

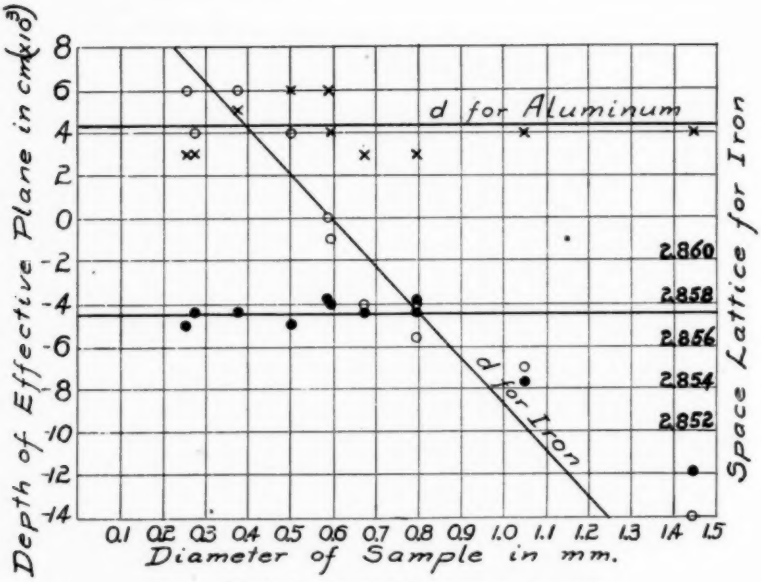

Fig. 2. Variation of d with diameter of sample.

The results of the last column of Table III are also plotted as a function of diameter in Fig. 2 using black dots, and here it is worth while noting that the points are closer to a straight line up to 0.8 mm than are the points for the other two curves. As shown by Table III the edge of the iron cube is 2.8575 within one part in 15,000, taking the mean wavelength of the Kα doublet of molybdenum as 0.71000A, which is the mean value given by Duane[6] as accurate to 1 part in 35,000.

Chemical analysis of the iron used in investigating the effect of sample diameter upon spacing measurements showed the iron to have carbon as an impurity. Hence this iron was checked in two ways against Burgess pure electrolytic iron which is purer than Baker's analyzed iron wire used for standardization purposes and contained no carbon whatever.

[6] Duane, Nat. Res. Coun. Bull. **1**, Pt. 6, p. 394.

First, both specimens of iron were inserted in the same sample tube and an exposure made. Second, the pure iron was run against pure sodium chloride as a standard. The results were 2.8605 and 2.8601 (mean 2.8603) on the Duane standard of wave-length.

An inspection of Table II shows that unless one desires to press the degree of accuracy to that given in this paper he will make but a small error in his result by ignoring entirely the diffraction lines nearest the center of the film and taking the mean of the last three or four lines only, provided the ratio of the radius of the camera to that of the sample is at least 500; for it will be noted that the mean of the readings for the faces 220, 310, 222 and 321 for the first three rows of Table II is 2.8581 which is not far from the true value for 0.7100A, viz., 2.8576. A second proviso here is, of course, that the camera radius is corrected for in the manner indicated.

Critical Discussion of Correction Factors in Powder Method

Hadding[7] has discussed the disturbances in the line distances and in the breadth of lines in the powder method and has derived the formula

$$2l_c = 2l - r_0(1+\cos 2\theta)$$

in which l and l_c have the meanings given in this paper, r_0 is the sample radius and θ the glancing angle. He states that this formula holds when the secondary (the diffracted) rays are excited only on the surface of the sample, i.e., for strongly absorbing substances. It should be noted that the correction for line distance is negative and varies from $2r_0$ to 0 as θ increases from 0 to $\pi/2$. Using Bragg's value for the space lattice of iron pyrites and the well known value for the lattice constant of rock salt, Hadding calculates the distance between corresponding lines and compares them with the measured distances on a film of camera radius 5.05 cm, getting differences varying from -1.9 mm to -1.1 mm for pyrites and -1.4 mm to 0.0 mm for rock salt, the diameter of the sample in both cases being 2 mm and a copper anticathode being used. He then remarks that for those cases where the rays penetrate further into the sample the difference between calculated and measured values lessens. It does not appear from his discussion that the correction factor can change sign as the writer has found it to do for iron as the sample radius changes. Hadding states that if the measurements for the double displacement are taken from the outer edges of the lines instead of from their centers that no correction is needed for absorption or penetration, but that there will always be a constant difference between calculated and measured line

[7] Hadding, Centralblatt f. Min. etc. p. 631 (1921).

distances equal to the diameter of the sample. Hadding therefore states the following rule: Measure all line distances from the outer edges of the lines and subtract the sample diameter from each of these distances. No support of the rule is given from experimental measurements.

It was deemed worth while to test Hadding's rule in the case of one of the films for aluminum and iron, so one out of several films taken for sample diameter 0.798 mm was chosen. The centers of the lines were carefully measured as were also their outside edges, these measurements

TABLE IV

Comparison of methods of correction for penetration

Blake's method

Aluminum ($d_1 = .002$)				Iron ($d_2 = -.004$)			
Face	l	l_c	r_c	Face	l	l_c	a_c
111	5.051	5.064	16.588	110	5.887	5.865	2.8525
200	5.839	5.850	16.574	200	8.337	8.321	2.8585
220	8.302	8.310	16.559	211	10.278	10.265	2.8535
311	9.793	9.800	16.586	220	11.923	11.912	2.8554
222	10.244	10.250	16.586	310	13.408	13.399	2.8546
400	11.882	11.887	16.565	222	16.066	16.059	2.8523
331	13.012	13.017	16.575			Mean:	2.8544
420	13.371	13.376	16.577				
422	14.727	14.731	16.567				
333	15.700	15.704	16.577				
		Mean:	16.575				

Hadding's method (radius of sample = .040)

Aluminum				Iron			
Face	l	l_c	r_c	Face	l	l_c	a_c
111	5.115	5.075	16.624	110	5.923	5.883	2.8520
200	5.912	5.872	16.636	200	8.385	8.345	2.8587
220	8.385	8.345	16.629	211	10.325	10.285	2.8563
311	9.883	9.843	16.658	200	11.981	11.941	2.8568
222	10.306	10.266	16.612	310	13.501	13.461	2.8501
400	11.950	11.910	16.597	222	16.144	16.104	2.8526
331	13.100	13.060	16.630			Mean:	2.8544
420	13.451	13.411	16.620				
422	14.810	14.770	16.611				
333	15.788	15.748	16.623				
		Mean:	16.624				

being taken $2\frac{1}{2}$ months later than the first measurements on the film. The results are shown in Table IV. In this table many of the headings are the same as in Table I. Following Hadding's rule for measurements by his method $l_c = l - r$ where r is the sample radius. The agreement for the space lattice is seen to be exact although the individual readings differ somewhat. It should be noted that the so-called radius of the camera was by the method of this paper 16.575 cm, by Hadding's method 16.624 cm,

and that the maximum variation from the mean for this radius was somewhat greater in Hadding's method. A further check on Hadding's method was made on the sample of diameter 0.378 mm and the two methods agreed to within 0.07 percent. However, the maximum variation in the radius of the camera by Hadding's method was 0.38 percent while by the method here reported on it was only 0.11 percent. On the iron lattice the maximum variations by the two methods were respectively 0.35 and 0.19 percent. It seems to the writer that Hadding's method is bound to give considerable variations in quantities that one ought to expect to be constant for the reason that the width of a line is dependent upon its intensity. It ought to be stated that when the indicator line of the comparator was put on the outside of even the most intense line of any film it was easy to note with the unaided eye that the point of maximum intensity was considerably removed from this edge.

The writer regards this agreement between the two methods as a strong support of the ideas concerning penetration contained in this paper. He wishes to emphasize the fact that the correction factor may be either positive or negative, depending upon the thickness of the sample. Over a wide range it is always positive for elements of low atomic number like aluminum and sodium, always negative for heavy elements like lead. As shown for iron, it changes sign for intermediate elements.

A Second Correction Factor*

If one plots against the glancing angle the space lattice of iron as given for each line in Table III, the fact is revealed that the correction factor $d \cot \theta$ tends to make the value of the lattice constant slightly too large for the first two lines and slightly too small for the next three. The difference is slight but beyond the limits of error so an attempt has been made to find a correction factor in an entirely different way.

It is well known that the absorption of x-rays is proportional to the third power of the wave-length. Suppose both edges of any line on the film are measured. Call A the absorption. Then it follows from the law of absorption that $\delta A/A = 3 \cot \theta \, \delta\theta$, since the wave-length varies as $\sin \theta$. This means that for substances that are easily penetrated (d positive) the inner edge of each line is displaced by an amount which is proportional to $\delta A/A$ toward the direction of smaller values of θ. Thus, the true correction factor should be proportional to $\cot \theta \, \delta\theta$.

Suppose on the other hand that the rays are only very slightly penetrating. Then, following Hadding, an amount $\delta l = r$, the radius of the

* This section was added May 18, 1925—Ed.

sample, should be subtracted from all readings on the film. In the case of a sample that is partially penetrated by the rays, obviously, the proper correction consists of two parts, one depending upon penetration and the other depending upon absorption; and there is evidently a mean condition of no correction where these two corrections balance each other (equivalent to saying $d=0$).

An attempt has been made to apply the alternative correction to the aluminum lines for the second sample of diameter 0.798 mm of Table III. This method wholly eliminates the slight lowering of the space lattice obtained from the middle lines spoken of above and so may be regarded as an improvement.

The bearing of the ideas presented in this paper upon the question of the so-called index of refraction of substances to x-rays will be discussed in another paper.

Cordial acknowledgement is made to the Board of Trustees of the University and to the American Association for the Advancement of Science for financial assistance in this investigation.

MENDENHALL LABORATORY OF PHYSICS,
OHIO STATE UNIVERSITY,
March 19, 1925.

THE SCHOTTKY EFFECT IN LOW FREQUENCY CIRCUITS

By J. B. Johnson

Abstract

(1) *In the absence of space charge.* This effect, discovered by Schottky, which depends on the probability fluctuations of electron emission from a filament, has been measured over a considerable range of conditions in resonant circuits of which the natural frequency was varied from 8 to nearly 6000 p.p.s. The effect is much larger in the lower range of frequencies than the theory predicts. *With a tungsten filament,* the ratio of observed to theoretical effect e'/e is about .7 for frequencies above 200, but increases rapidly to 50 at 10 cycles per sec. *With an oxide coated filament,* the ratio increases from 1 at 5000 cycles to 100 at 100 cycles. This is interpreted to mean that the emission of electrons is not strictly chaotic but is influenced by irregular temporal changes in the cathode emissivity. In a high frequency circuit these changes become imperceptible and the emission is effectively random. (2) *When current is limited by space charge* the Schottky effect decreases because of the interaction of the electrons, and other disturbances may act upon the space charge so as to completely mask the remanent Schottky effect. The magnitude of the disturbances in amplifying vacuum tubes can therefore not be predicted from measurements on the true Schottky effect.

THE thermionic current in a vacuum tube is not a smooth flow of electricity, but is subject to rapid and irregular fluctuations in magnitude. These fluctuations, discovered by W. Schottky and called by him the "Schrot-Effekt" (small shot-effect) are caused by the *random* emission of electrons from the cathode, and are made manifest by voltage or current fluctuations in any circuit into which the tube is connected. When these irregularities are sufficiently amplified by other vacuum tubes to be perceivable by means of a telephone receiver, they give rise to a continual sound with no definite pitch, like that usually associated with the conch shell, or like the faint sound that is heard when the hand is cupped to the ear.

The mathematical theory of the Schottky effect[1] is based upon the assumption that *the electrons pass from the cathode to the anode of the tube independently of one another.* Interpreting this condition by the simple laws of probability, it has been shown that the magnitude of the fluctuations of voltage or current in the circuit associated with the tube should depend only upon the charge on the electron, the average space current,

[1] W. Schottky, Ann. der Phys. **57,** 541 (1918); idem. **68,** 157 (1922).
J. B. Johnson, Ann. der Phys. **67,** 154 (1922).
T. C. Fry, J. Franklin Inst. **199,** 203 (Feb. 1925).

and the circuit constants. This prediction has hitherto either failed of verification[2] or has been verified only in part.[3]

It is the purpose of this paper to present the results, first, of a considerable series of measurements on the Schottky effect as it appears in circuits of comparatively low natural frequency, and secondly, of some preliminary studies upon the possible relation between the Schottky effect and the "noise" in vacuum tube amplifiers.

The measurements made under the conditions in which the Schottky effect should appear, i.e., in two electrode tubes with no appreciable space charge, show some striking deviations from the theory. While in the higher range of frequencies that were studied or with very low space currents the effect approached the predicted value, at the lower frequencies it is much too large. Particularly interesting is the behavior of oxide coated cathodes which give an effect up to hundreds of times too large at the lowest frequency, remarkable when we consider that this state of affairs can only be caused by a sequence of electron emissions different from the postulated purely random one. Except for the fact that this larger effect varies with the frequency and the space current, the circuit responds to it much the same as to the purer Schottky effect at the higher frequencies.

In amplifier tubes on the other hand, space charge is always present and makes the electrons pass in a sequence more orderly than the purely chaotic one. In fact, in these tubes the Schottky effect is so profoundly affected by the presence of space charge that even in the same tube there is little correlation between the noise with and without space charge. Furthermore, when space charge limits the current in a tube the opportunity also exists for agencies to come into play that can alter the current by acting upon the space charge. Tungsten filament tubes are usually subject to disturbances of this kind, so large and frequent that they entirely mask the reduced Schottky effect. Wehnelt cathodes are much less productive of this kind of disturbance so that consistent measurements can be obtained with tubes having oxide coating filaments.

The measurements here reported were done with apparatus in which the final indicating instrument was a thermocouple and micro-ammeter. Since the measured effect did not in general agree with the theory, the

[2] C. A. Hartmann, Ann. der Phys. **65,** 51 (1921); Phys. Zeits. **23,** 436 (1922). Hartmann's method of measurement could not give correct results, as pointed out by R. Fürth (Phys. Zeits. **23,** 354, 1922).

[3] A. W. Hull and N. H. Williams, Science, Aug. 1, 1924, p. 100; Phys. Rev. **25,** 147 (Feb. 1925). These authors obtained a check with the theory using a circuit of high natural frequency.

measurements were carried out for a number of tubes and covered a considerable range of frequencies, current values and circuit constants. The evaluation of the data was done according to the exact relation derived by Fry rather than by the approximate formula of Schottky.

Method of Measurement and Computation

For the purpose of measuring the Schottky effect the space current of the tube was passed through the inductance and resistance of a damped resonant circuit. The voltage fluctuations set up across this circuit were amplified with comparatively small distortion, by an amplifier[4] which terminated in a vacuum thermocouple and micro-ammeter. The measuring system therefore indicated the effective square of the voltage surges over the resonant circuit.

This measuring circuit, comprising the amplifier and thermocouple, was calibrated by sinusoidal alternating voltage over the whole range of frequencies of the variable resonant circuit, extending from about 8 p.p.s. to nearly 6000 p.p.s. The calibrating voltage was obtained from a vacuum

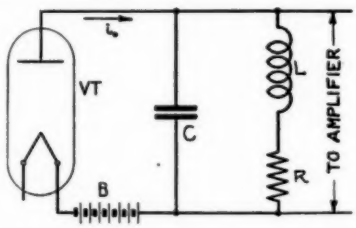

Fig. 1. Experimental circuit.

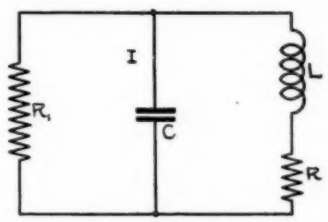

Fig. 2. Equivalent experimental circuit.

tube oscillator and was attenuated to the necessary small fraction of a measured initial value by a two-step resistance potentiometer. The resistances in this network were arranged and shielded with special care with a view to avoiding induction effects between the branches.

The circuit immediately connected to the experimental tube is shown diagrammatically in Fig. 1. The tube itself is represented by VT, B is a dry cell battery, usually of 360 volts, while L, C and R are the inductance coil, condenser and resistance in the resonant circuit. The condenser C was a mica condenser of negligible effective resistance. It was variable in steps from $1\mu f$ to $.001\mu f$. For the lowest frequencies this was supplemented by paper condensers of up to $7.5\mu f$ capacity of known effective resistance. The resistance R was a non-inductive decade box. For the

[4] The amplifier consisted of four stages with Western Electric 102-D tubes and one stage using a 101-D tube, all resistance-capacity coupled. The total voltage amplification was about 3×10^5 and the power amplification was 10^{14}.

inductance L four separate coils were used, each calibrated over the pertinent range of frequency and direct current value for effective inductance and series resistance. One of these coils, A, whose inductance was .100 h, was wound on a toroidal wood core. The other three were wound on cores of silicon steel with air gaps, and their inductances were about .1 h, .025 h, and 38 h, respectively and will be referred to as coils B,C and D.

The experimental circuit includes also the input elements of the amplifier, but electrically it can be represented by Fig. 2. In this diagram R_1 is the resultant of three resistances in parallel, namely, the resistance to alternating current of the experimental tube at any particular condition, the grid leak resistance of the first amplifier stage and the effective input shunt resistance of the tube in this stage. In the value of C must be included also the input capacity of the first amplifier stage, usually negligible. These various values were obtained by suitable measurements.

The measurements that were made upon the Schottky effect in this circuit will, in what follows, be expressed in terms of the mean square voltage $\overline{V^2}$(obs.) across the resonant circuit at the input of the amplifier. This quantity is given simply by the product of the deflection of the thermocouple meter (less the zero reading caused by inherent amplifier noise) and the calibration constant of the measuring system, which was calibrated in terms of voltage squared.

This measured quantity is to be compared with the corresponding quantity $\overline{V^2}$(calc.) which is obtained from the known conditions and circuit constants as shown by Fry.[1] Fry has developed a general formula for the Schottky effect which is applicable to any circuit. However, the specific example given by Fry covers exactly the arrangement of apparatus shown in Fig. 2, so that his Formula (13) can be used directly in this case. With certain changes in the notation,[5] made for convenience in the presentation, this formula reads,

$$\overline{V^2}\,(\text{calc.}) = \frac{ei_0}{2C^2}\,\frac{L}{R(1+L/RR_1C)}\left[1+\frac{C}{L}\,\frac{R^2}{(1+R/R_1)}\right].$$

in which

e = charge on the electron;
i_0 = average space current;
L = effective inductance;
C = total capacity;
R = effective resistance in the inductance branch;

[5] Fry's formula is expressed in terms of S, the mean power in the thermocouple, instead of the mean square voltage over the resonant circuit.

R_1 = total shunt resistance, including that of the experimental tube, grid leak and amplifier tube.

Great accuracy was not striven for in this work because of the large differences found to exist between measurements and theory. Taking into account all the possible sources of error which could enter the observations, calibrations and measurements of circuit constants, the probable error of a single comparison between an observed and a calculated value of V^2 is about five percent.

Procedure and Results

For certain preliminary work the thermocouple in the measuring circuit was replaced by a pair of telephone receivers which could also be connected to a variable source of current giving a sound similar in character to that produced by the amplifier. By the use of this modified circuit a considerable number of tubes were examined under identical conditions in order to determine qualitatively the influence of structural factors upon the amplitude of "noise" produced when the space current is limited by the cathode temperature so that space charge is practically absent. These tubes differed from one another, in the first place, as to the arrangement of the electrodes, some being standard audions while others were special tubes having the cathode and anode in various dispositions. Some of the tubes had the electrodes insulated with extreme care, and one tube had the electrodes enclosed in a grounded metal cylinder so that no part of the glass was exposed to the light or the electron current from the filament. The anode material was nickel in most of the tubes, but in some platinum or tungsten was used. The tubes had filaments of different materials such as platinum coated with rare earth oxides by various methods, commercial tungsten, pure tungsten and single crystal tungsten.

In the amplitude of sound which they produced these tubes differed from one another considerably, by factors perhaps as large as ten. Among all the variables, however, only that of the filament material showed a definite correlation to the sound. The sound from the tubes with oxide coated filaments was on the average several times larger than that from the tungsten filament tubes, but of the same quality so far as could be judged. In one tube the gas pressure was varied while the sound was observed, but there was no appreciable increase in the loudness until the pressure was so high that a glow began to be visible in the tube. In another case the tube was exposed to various amounts of illumination without any effect on the sound.

From the tubes thus tested, three were selected as representative of their groups, for the quantitative measurements. Two of these tubes were standard Western Electric 102-D audions with plane-parallel plates and grids and a V shaped ribbon of oxide coated platinum as cathode. These will be referred to as tubes No. 2 and No. 3. Tube No. 1 was similar in structure but had a filament of pure tungsten. When they were used as two-electrode tubes the grid and plate were connected together so as to form but one anode.

The results of the observations on these tubes will be presented so as to show the relation between the observed and the calculated value of $\overline{V^2}$, first as the circuit constants C, L and R, the natural frequency of the resonant circuit, and the space current i_0, are varied in the absence of space charge; and secondly, as space charge limits the current in the two-

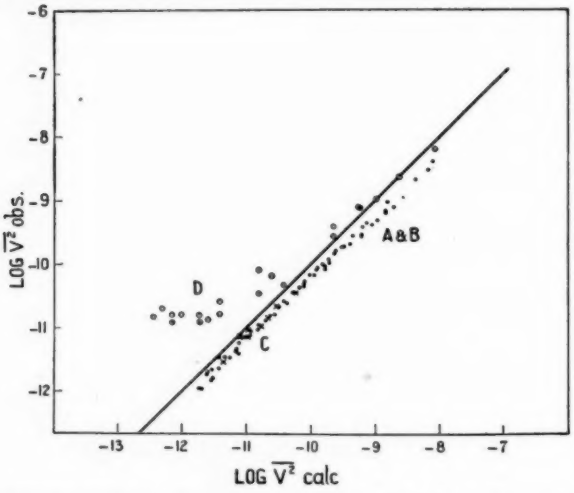

Fig. 3. Capacity and inductance variation for tube No. 1, tungsten filament; current 5 m-a.; various inductances A, B, C and D; frequency 8 to 6000 p.p.s.

electrode or three-electrode tube. The solid line in the diagrams is in each case the locus of the theoretical value of $\overline{V^2}$. The letters A, B, C and D on the diagrams refer to the inductance coils that were used in the resonant circuit for the groups of points which the letters designate.

A. The Schottky Effect in the Absence of Space Charge

In Figs. 3 and 4 is shown the relation of the observed to the calculated values of $\overline{V^2}$ for tubes No. 1 and No. 2 respectively, the capacity of the resonant circuit being varied between the limits 7.5μf and .01μf. The observations for the tungsten filament tube with the smaller inductance lie nearly parallel to the theoretical line but somewhat below it, as if the

charge of the electron were about two-thirds of what it is known to be. With the 38 henry coil the observed values of $\overline{V^2}$ become increasingly too high with increasing capacity, being about 50 times larger than the

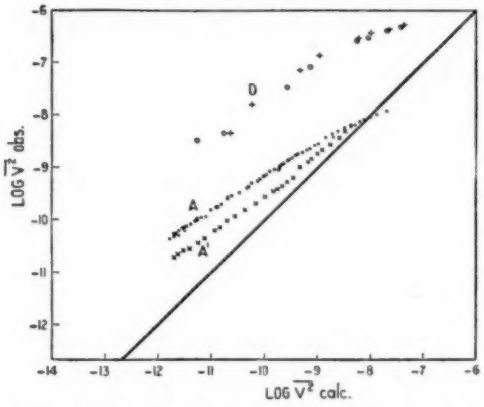

Fig. 4. Capacity and inductance variation for tube No. 2, coated filament; current 5 m-a.; two inductances A and D. Curve A′ was taken at a different time.

theoretical value at the largest capacity. The oxide coated filament tube yielded values that are too high over nearly the entire range and approach the theoretical values only at the lower capacities. Oxide filaments also

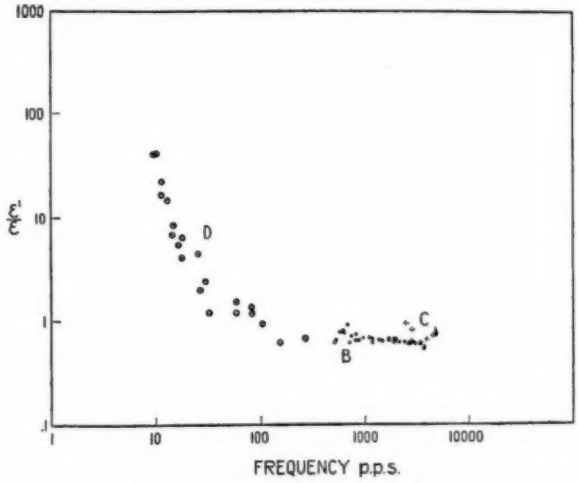

Fig. 5. Frequency variation for tube No. 1, tungsten filament; same data as in Fig. 3 plotted to frequency scale.

show a greater change with time than has been observed with tungsten filaments, as illustrated by the curves A and A′ of Fig. 4, obtained with the same tube under identical conditions but at different times.

The variable which causes the divergence from linearity of the curves of Fig. 3 and Fig. 4 and which does not appear in the theory is the frequency of the resonant circuit. This is definitely shown upon plotting to a frequency scale, as has been done for the previous data in Figs. 5 and 6, and in Fig. 7 for other data. The ordinates are the ratios of the apparent to the actual charge of the electron, which is the same as the ratio of the observed to the calculated values of $\overline{V^2}$. The logarithmic scales of Figs. 5 and 6 cover a larger range, while the linear scale of Fig. 7 brings

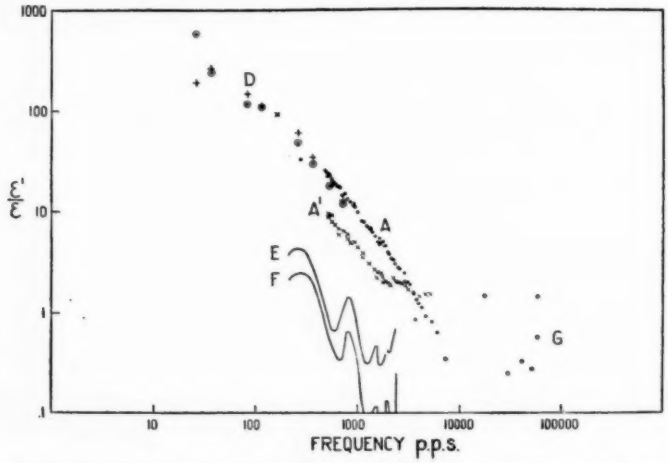

Fig. 6. Frequency variation for tube No. 2, coated filament; same data as in Fig. 4 plotted to a frequency scale; curves E and F give Hartmann's results for 2 m-a. and 20 m-a.; points G were obtained with less steady measuring circuit.

out more strongly the course of events in the higher frequency range. The fact that the curves obtained with the various inductances join up where they overlap in frequency shows clearly that the *frequency* of the resonant circuit is the determining factor in the large discrepancy between observation and theory.

The points marked G in Fig. 6 were obtained with a less reliable circuit and are included merely to show that the order of magnitude, at least, of the observed ratio does not lie far from unity up to the natural frequency of 100,000 p.p.s. The solid lines E and F in the same figure are plotted, for a comparison, from Hartmann's data for a tantalum filament at the space currents of 2 milli-amperes and 20 milli-amperes.[6]

Even when the ratio of the observed to the calculated value of $\overline{V^2}$ is considerably larger than unity, it is still independent of the effective damping resistance in the resonant circuit. Fig. 8 presents a series of

[6] C. A. Hartmann, Phys. Zeits. **23**, p. 436 (1922).

observations in which the resistance R was varied from 29 ohms at the upper end of the curve to 1029 at the lower end. This last value is about half the critical damping resistance of the circuit, and yet the points lie on a straight line within the errors of measurement.

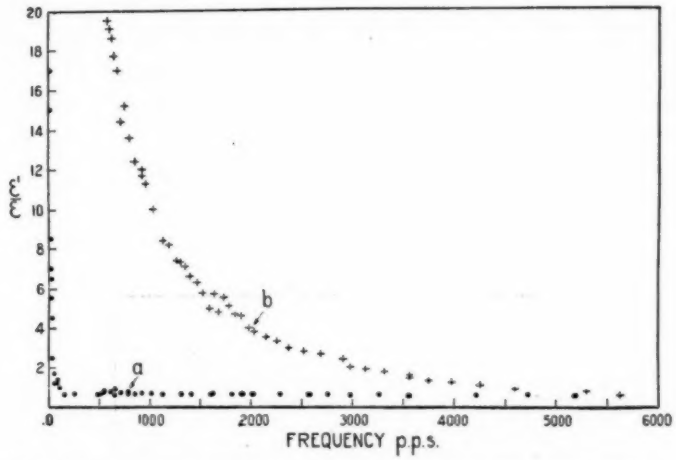

Fig. 7. Frequency variation plotted to a linear frequency scale.
a. Tube No. 1, tungsten filament; inductance A; current 5 m-a.
b. Tube No. 2, coated filament; inductances B and D; current 5 m-a.

The curves of Figs. 3 to 8 have to do with the dependence of the observed effect upon the circuit constants and show that except in so far

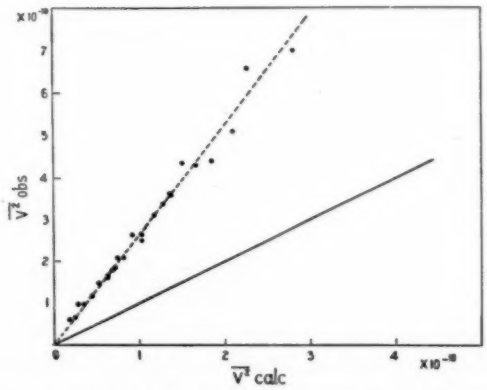

Fig. 8. Resistance variation for tube No. 3, coated filament; inductance A; capacity .07μf; frequency 1900 p.p.s.; current 5 m-a.; resistance 29 to 1029 ohms.

as the circuit constants determine the *frequency* of the circuit their influence is that predicted by the theory. This fact, as well as that different tubes give different results, shows that the deviations of the observed

ratio from unity is not caused by failure of the theory to use the circuit constants correctly but by the inadequateness of the original assumptions at the basis of the theory.

Curves relating the observed and calculated voltage fluctuations as the space current is varied throw interesting light on the subject of these deviations, especially again in the case of the oxide coated filaments. Fig. 9 gives two such curves for a tungsten filament, and Fig. 10 gives a series of curves obtained with an oxide coated filament, the space current being controlled by the filament temperature. In the measurements on the tungsten filament tube the current i_0 ranged from 10 milli-amperes to .01 milli-ampere, and in this thousand-fold range there is no marked deviation of the curve from linearity although the observed values are

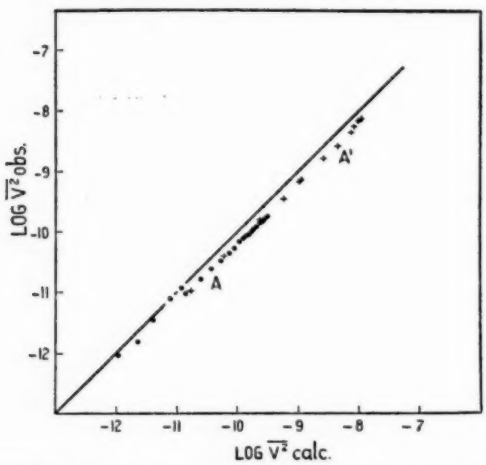

Fig. 9. Current variation for tube No. 1, tungsten filament; inductance A; capacity .10μf for A, .01μf for A_1; frequency 1590 and 5300 p.p.s.; current 10 to .01 m-a.

low by about the same amount as they are in Fig. 3. Experimental obstacles prevented getting a curve at the low frequencies where, as in Fig. 3, the observed $\overline{V^2}$ is much too high.

In the corresponding curves for the oxide coated filaments, Fig. 10, the space current range was from 5 milli-amperes down to .1 milli-ampere in most cases. The remarkable feature about these curves is that they all approach the theoretical line as the space current is decreased. It is as if with decreasing current, or perhaps decreasing filament temperature, the ideal conditions were approached which are assumed in the theory and which for the same current values more nearly exist in the tungsten cathode tubes.

B. Schottky Effect and Space Charge

The modification of the Schottky effect caused by the appearance of space charge in a two-electrode tube is shown typically in Fig. 11. For this

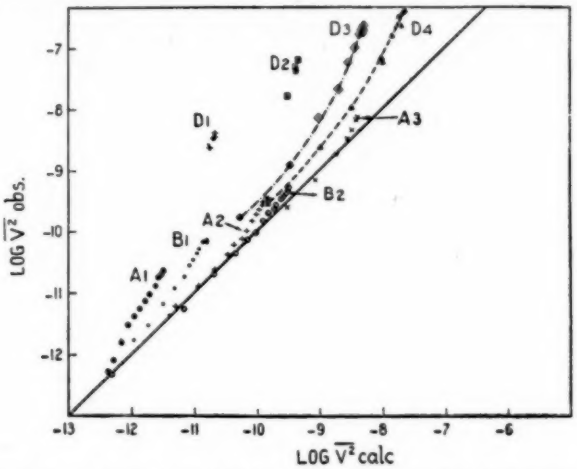

Fig. 10. Current variation for tube No. 2, coated filament; inductances as shown by letters; capacities A_1, .80μf; A_2, .10μf; A_3, .010μf; B_1, .20μf; B_2, .02μf; D_1, 1.00μf; D_2, .10μf; D_3, .0101μf; D_4, .0022μf; current range 5 to .1 m-a.

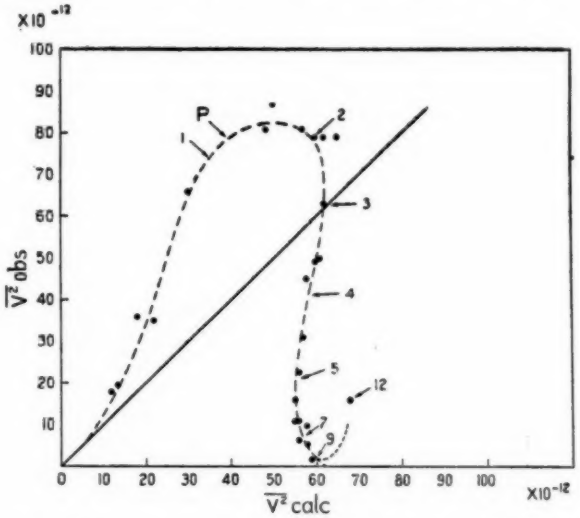

Fig. 11. Effect of space charge for tube No. 2; inductance A; capacity .10μf; frequency 1590 p.p.s.; current in m-a. given by figures.

experiment the anode potential was reduced to 9 volts and the space current was controlled by the cathode temperature. The space current values, in milli-amperes, are indicated by the figures attached to the

arrows. The curve relates to tube No. 2, with oxide coated filament. As was the case with the higher anode voltage the observed values of $\overline{V^2}$ increase faster than the calculated. At the current of one milli-ampere, however, space charge begins to be appreciable and the observed values of $\overline{V^2}$ decrease until at 10 milli-amperes it is a small fraction of the calculated value.[7] Above ten milli-amperes[8] the observed values again increased and became very erratic, and the sound when heard in the telephone was characteristically changed.

Tungsten filament tubes show this effect of increasing noise in the space charge region to a much larger degree and at a much sharper limit. At the current value where the effect of space charge is just discernible on the space current-temperature diagram, corresponding to the point P in Fig. 11, current pulses begin to be superimposed on the more regular Schottky effect. These become more frequent as the filament temperature is increased until thermocouple measurements are difficult or impossible. An attempt to estimate the magnitude of these pulses was made by comparing them with the effect of discharging a small condenser through some part of the circuit. The estimates indicated that the pulses were equivalent to the passage, or the failure to pass, of a charge of 10^5 to 10^8 electrons.

If these current pulses were produced by the sudden emission, or failure of emission of a group of electrons from the filament they would, like the Schottky effect, be most distinct in the absence of space charge and would be suppressed in the space charge region. Since the opposite is the case they must be caused by something which acts upon the space charge and thereby varies the current. The evidence points to the conclusion that the "clicks" are caused either by ions which pass through the space charge or by ions which are held in the space charge region near the filament for some time. In the case of a current pulse of 10^8 electrons, a calculation shows that this could be produced by the passage from the filament to the plate of 2.3×10^6 hydrogen ions, of 1.7×10^5 singly charged tungsten atoms or of one singly charged tungsten particle 2×10^{-3} mm in diameter. The large size of the particle seems to rule out the last hypothesis, but there is as yet no other discriminatory evidence.

The phenomena which space charge introduces in the two-electrode tube are also present in the three-electrode tube where the current is

[7] The calculated value of $\overline{V^2}$ fails to rise linearly with increasing space current because of the lowered internal resistance of the tube, which in turn greatly lowers R_1.

[8] The saturation current for the oxide coated filament is not well defined, and the higher currents were reached by heating the filament considerably above the normal temperature.

controlled largely by the artificial space charge of a grid. Fig. 12 contains the data obtained with the tungsten filament tube No. 1, plotted similarly to those of Fig. 11 for the two-electrode tube. The space current, denoted as before by the figures attached to the arrows, was controlled by the filament temperature. As in the case of the two-electrode tube the noise decreases with the appearance of space charge, but here only to about one-third of the theoretical value as against nearly zero for the two-electrode tube. The fluctuation which remains, however, gives rise to a sound in a telephone of the same character as does the pure Schottky effect and is no doubt a Schottky effect which is modified by the space

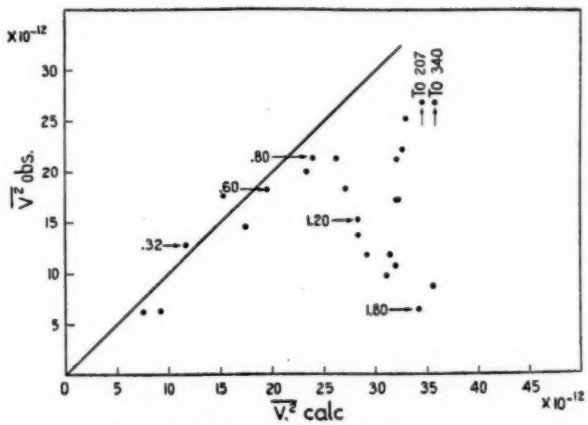

Fig. 12. Space charge in three-electrode tube No. 1; inductance A; capacity .10μf; current in m-a. given by figures.

charge. This conclusion seems supported by the fact that there is a relation between the noise a tube produces and the amplification as measured in the same condition, such that the ratio of noise to amplification is never less than a certain value. This is made clear by Fig. 13 in which each circle indicates in arbitrary values the measurement of noise and of amplification of one tube. A wide variety of tubes were used for this set of measurements. The circles of the diagram lie to the right of a straight line through the origin with only one or two exceptions. It seems probable that this line represents the residual of the Schottky effect in tubes when other disturbances are absent.

The inherent "noise" in vacuum tube amplifiers cannot, therefore, be estimated by the theory of the Schottky effect as it now stands. This is so partly because the theory has not been extended to take into account the presence of space charge, and still more because the remanent Schottky effect is usually masked by other disturbances which become effective when space charge appears.

Discussion

The experimental results cited here give force to the contention of Fry[1] that the Schottky effect is not a proper means for measuring the charge on the electron. It is rather a phenomenon which enables us, with the aid of *the already known value of e*, to determine the truth or falsity of the basic assumptions underlying the theory. The assumption which has the least foundation on previously known facts, instinctive though it may be, is that which concerns the random emission of electrons, and it is to this assumption that the test of the experiments should be, and here has been, applied. The discrepancies existing between theory and experiments, with the striking introduction of the frequency as an independent vari-

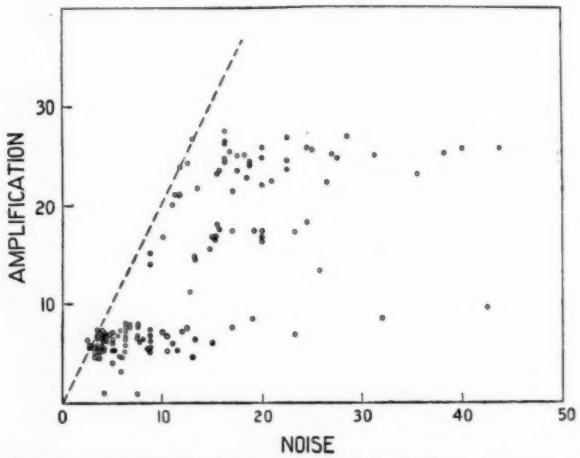

Fig. 13. Amplification as a function of noise in three-electrode tubes; noise in arbitrary units; each point represents a tube.

able, are clearly caused by the fact that the electron emission does not strictly follow the chaotic sequence assumed in the theory. However, since this deviation takes a much simpler course than Hartmann's results indicated, it yields to an explanation which seems more plausible than that offered by Hartmann and Schottky.[9]

The Hartmann-Schottky hypothesis is that the cooling produced on a small surface of the cathode by the emission of one electron makes the emission of another electron from the same area less probable for a time comparable with the natural period of the resonant circuit. The present data, however, do not show the maxima and minima in the $\overline{V^2}$-frequency curve that are so prominent in Hartmann's curves (Fig. 6). Further-

[9] C. A. Hartmann, Ann. der Phys. **65,** 51 (1921);
W. Schottky, Ann. der Phys. **68,** 157 (1922).

more, although such low frequencies were attained (down to 8 p.p.s.) that the time required for the small surface cooled by the emission of one electron to reach equilibrium must be very small compared with the period of the circuit, yet even at this low frequency the ratio of the observed to the calculated quantity was rising rapidly. The above hypothesis seems, therefore, to be no longer either necessary or tenable.

An assumption of a somewhat different nature leads to conclusions which agree better with the facts. We may suppose that the chance of an electron emission is influenced not so much by previous emissions as by other factors which change irregularly with the time, chiefly the activity of the filament. The electron emission at any time depends upon the condition of the cathode surface, and the surface is probably in a continual process of change due to such causes as evaporation, diffusion, chemical action, structural rearrangements and gas ion bombardment. These changes would go on at different rates in different parts of the surface and would cover areas very large compared with that involved in the emission of one electron. The changes involving the greater area or larger amplitude might be expected to require a longer time, while changes so small as to affect only a few electrons would lose their significance in the general statistical emission. The general effect of these changes would be a variation in the total space current superimposed upon the fluctuation of the Schottky effect, having little influence at the high frequencies and an increasing effect as the natural frequency of the measuring circuit becomes lower. Again, the effect might well be greater for the composite surface of an oxide coated cathode than for one of a relatively pure metal, and the effect might be more dependent upon the temperature with a cathode of the former type.

The sum of these considerations, therefore, seems favorable to the view that the large discrepancies between theory and experiment at the lower frequencies are caused by secular changes in the surface conditions of the cathode. The values of $\overline{V^2}$ which are too low, on the other hand, sometimes as low as one-fifth of the theoretical value, require a different explanation, but no adequate explanation has been found.

BELL TELEPHONE LABORATORIES, INCORPORATED,
NEW YORK, N. Y.
January 8, 1925.*

* Received April 11, 1925—Ed.

NON-MAGNETIC FILMS OF NICKEL

By L. R. Ingersoll and S. S. De Vinney

Abstract

Properties of sputtered nickel films.—(1) *Magnetic.* These films, prepared by sputtering in hydrogen on to a cooled surface, with a 1000 volt d.c. generator, are initially non-magnetic, showing neither magneto-optic rotation nor tractive effects in a magnetic field. After heating to 300° or 400°C, however, they become strongly magnetic and exhibit both these effects. Films much thicker than 120mμ, or those sputtered with an induction coil, are likely to be magnetic from the start. (2) *Crystal structure.* X-ray spectrograms by the powder method show for the heat-treated (magnetic) film the face-centered cubic lattice as for ordinary nickel, but prove that the original non-magnetic film is amorphous. These facts suggest that *ferro-magnetism* in nickel, at any rate, is not a property of the individual atom as customarily supposed, but of the crystalline aggregate. A number of possible objections to this point of view are taken up and discussed. (3) *Electric.* The gain in magnetic properties on heat-treatment is accompanied by a decrease of *resistance* to a fraction (a fifth in one case) of its initial value. The original film also gives only about 1 percent of the *Hall effect* that it does after heat-treatment. (4) *Color.* Some films, particularly those deposited on a surface at liquid-air temperatures, display remarkable colors. On examination of the reflected light with a spectroscope, only a narrow spectral region is seen to be absent. If the nickel films are thin, covering with an optically dense liquid completely destroys the colors.

SOME years ago one of the writers noticed that most films of nickel sputtered in hydrogen showed little or no Faraday or Kerr magnetic rotation. On taking up the matter later it was found that these films which gave no magneto-optic rotation also *showed no tractive effects* when suspended in a magnetic field, although after heating to a few hundred degrees for a short time both magneto-optic and tractive effects appeared.

As this "non-magnetic nickel," if such it can be considered, has seemed of more than passing interest, and the change to the magnetic form produced by heating is so striking, considerable study has been devoted to it and the results will be described briefly.

Preparation of films. These were deposited with the apparatus described in a recent paper,[1] the chief novelty of which was the arrangement for keeping the surface (microscope cover-glass) on which the film was sputtered, cooled by running water or even liquid air. The cathode was a 32 mm disk cut from a plate of very pure nickel furnished by the International Nickel Co., through the kindness of Dr. Paul D. Merica. The

[1] L. R. Ingersoll, J. Opt. Soc. Amer. & R. S. I. **8**, 493 (1924)

analysis was given as: nickel, 99.48 percent; cobalt, 0.40 percent; iron, 0.10 percent; copper, 0.02 percent.

While an induction coil was used in some cases, the fifty or more best films were deposited with a direct-current generator at about 900 to 1000 volts. The cathode was 15 to 18 mm from the glass and the vacuum such that the dark space extended almost to its surface, the current being 15 to 20 milliamp. Save for a few experiments with nitrogen, the residual gas in all cases was hydrogen.

Magnetic tests were admittedly very primitive but quite satisfactory for the purpose. After sputtering, the film was cut into strips about 5×25 mm and one of these was suspended by a thread so as to swing freely between the poles of an electromagnet giving a field of some 12,000 gauss. The tractive effects when the current was turned on were observed and estimated on a scale of 1 to 100, the former representing the smallest observable motion and the latter about the magnitude one would expect for ordinary nickel; that is, an effect such that the film would instantly be drawn to one of the pole pieces. In making these estimates account had to be taken of the width and relative thickness of the film, factors which would make really accurate measurement a difficult problem.

Heat treatment was carried on at various temperatures between 100° and 450°C or higher, generally in a fairly good vacuum or low pressure (0.1 mm) hydrogen, although a few tests in hydrogen at atmospheric pressure and also in hot oil gave essentially the same results. The time element is quite secondary to temperature; a few minutes at 400° were much more effective than hours at 250°, while a few seconds in a Bunsen flame in air produced a large effect, although this was not easily controllable. A number of nickel films were sputtered over with a layer of gold and then heated. The surface then generally showed little blisters, indicating that the heat treatment involved an escape of gas (hydrogen) as would be expected. Some experiments were also tried on alloying with gold by sputtering this metal along with the nickel from a small strip across the cathode. The general characteristics were the same save that the gaining of magnetic properties upon heating was somewhat slower and not so marked. No substitute for heating, for bringing about magnetic properties, has been found. Ageing in a dessicator for six months or more produced little if any effect. Tests on ageing in a vacuum are not yet conclusive—3 months in vacuum seem to yield no results—although some effect might well be expected here from the experiments of Koller[2] on ageing platinum films in a vacuum. A trial of burnishing with a

[2] L. R. Koller, Phys. Rev. **18**, 221 (1921).

rounded glass rod, which might be expected to compact anything like a loose powder, brought about no magnetic effect.

Resistance measurements. The work of[3] Richtmyer and others shows that the resistance of a sputtered film generally decreases rapidly upon heating, so a like effect was to be expected for these nickel films. A test of a film the ends of which had been sputtered with gold to insure good contact, gave the following results:

Heat treatment	Resistance	Magnetic intensity
Original film	30.6 ohms	0
17 hr at 100°C	26.8	2
19 hr further at 150°	24.1	4
18 hr further at 200°	19.4	12
4 hr further at 250°	16.7	16
1.5 hr further at 300°	16.6	25
0.5 hr further at 350°	10.6	50
0.1 hr further at 400°	7.0	60
0.5 hr further at 450°	6.0	80

Other films showed qualitatively the same effects. If the heating at the higher temperatures was prolonged the film began to crack and the resistance rose. The change in resistance and in magnetic properties of the film tabulated above was probably almost complete.

Crystal structure. The powder method (G. E. apparatus, molybdenum tube) was used. The film was scraped from the glass with a sharp knife—it was usually strongly adherent and the scrapings resembled a fine black powder—and packed into the capillary tube. This was then tested in the magnetic field and showed no tractive effects. A 12 to 24 hr exposure was then made on it, after which it was heated to 400° for a short time and another exposure made. It was strongly magnetic after heating. Check films were also made on filings of metallic nickel and on a blank glass tube. The comparison substance in all cases was aluminum.

The photographs for the nickel filings and *heat-treated film* were practically identical and showed the face-centered cubic lattice as found by Hull[4] for this metal. *The original untreated nickel film, however, showed an amorphous character.* A second test, in which the nickel films used were especially carefully selected for their absence of any magnetic tractive effects, gave particularly conclusive evidence on this point.[5] Only the line produced by the (111) planes was present, indicating the presence of small groups containing only a few molecules each—not enough to produce interference of a higher order.

[3] F. K. Richtmyer and L. F. Curtiss, Phys. Rev. **15,** 465 (1920 ; L. F. Curtiss, Phys. Rev. **18,** 255 (1921); L. R. Koller, loc. cit.,[2] and others. See also F. W. Reynolds, Phys. Rev. **24,** 523 (1924).

[4] A. W. Hull, Phys. Rev. **17,** 571 (1921).

[5] Dr. Hull, who obligingly examined the x-ray films, considers that they prove beyond question that these nickel films are amorphous.

Other experiments. The films were ordinarily deposited in about half an hour and were usually almost opaque. Measurements by the interference method on an average film gave a thickness of about 120mμ. When the thickness was greatly in excess of this the film generally showed some magnetic properties from the start. In one case when the sputtering was continued for 20 hr the film was apparently as magnetic as ordinary nickel. This indicates that it would be difficult, if not impossible, to obtain this amorphous nickel in bulk form.

A number of films were sputtered with an induction coil, with varying results as regards magnetic characteristics. The rule seemed to be that the higher the potential used in sputtering the more likely the film was to turn out somewhat magnetic. A few films were sputtered in nitrogen but the results were unsatisfactory. The idea gained, on very little evidence, however, was that films deposited in this gas were likely to be magnetic.

Professor Alpheus W. Smith, who obligingly tested samples of both treated and untreated films for the Hall effect, reports that, while the measurements he was able to make left much to be desired in the way of accuracy, the indications were that the original film showed hardly more than 1 percent as much effect as the heat-treated one.

Color effects. Microscopic structure. In many cases, particularly when the surface on which the film was sputtered was kept at liquid-air temperatures, brilliant surface colors appeared. On examining the reflected light with a spectroscope it was found that only a narrow spectral region was absent, and that this absorption band moved towards the red with increasing film thickness. This duplicates almost exactly the observations of Wood[6] on sodium and potassium films. It is possible, however, to try certain things with nickel films which cannot be done with sodium and potassium and one of these is to cover with water or other liquid. It was found on trying this that, with thin films, liquids of low refractive index such as water dulled the color, while optically denser liquids like carbon bisulphide or mono-bromnapthaline completely destroyed it, although the color returned when the liquid was washed off. This might be construed in favor of Wood's theory that this absorption is a type of resonance phenomenon taking place in the interstices between the particles.

The matter of film color, however, is far from simple. In the thicker films the effect of the liquid was not as definite as explained above. Such films also occasionally showed evidence under the microscope of being double or triple in character after heat-treatment. In general an original film showed no trace of structure, while a heat-treated one frequently

[6] Phil. Mag. 38, 105 (1919)

showed a very complicated structure when examined with oil-immersion objective, although no connection could be clearly traced between this and the color effects. The colors were almost invariably changed by heating, sometimes disappearing and sometimes appearing when they did not exist before.

Discussion of Results; Conclusions

Undoubtedly the most important conclusion to be drawn from this work is that, on the evidence of these films, *ferromagnetism in nickel requires a crystalline structure and is therefore not a property of the individual atom, but of the crystalline aggregate.* Whether or not this means that the Amperian currents must circulate in orbits wider than the ones of atomic size customarily supposed, becomes a matter of interpretation, but the evidence would certainly seem to point in this direction.

There is a possible escape from this conclusion that the original film is non-magnetic because amorphous. As already mentioned, scrapings from such a film resemble a fine black powder. If this film, as originally deposited, could be regarded as a loose aggregate, its lack of magnetic properties might then be at least partially attributed to this fact rather than to its amorphous character. There are several reasons which have caused this point of view to be rejected: (a) The original film is tough and resistant, hard to rub off or scrape off. (b) Its optical properties are not at all such as one would associate with a loose powder. In appearance the film is bright and metallic-looking. The change produced by heating is small; it is slightly darker afterwards and has a faint golden tinge. (c) Its electrical resistance, while lessened by heat-treatment, is not high and indicates a coherent metal structure. Moreover, it cannot be assumed that the film is a compressed, rather than a loose powder, since the work of Speed and Elmen[7] on the magnetic properties of compressed powdered iron show a value of the permeability up to several hundred for this material.

Another possible suggestion, namely that the nickel as originally sputtered might be in an oxidized state and that the heat-treatment—usually carried out in hydrogen—involved a reduction of this to metallic nickel, may be answered at once by pointing out that heat-treatment could be effectively carried out in the oxidizing part of a Bunsen flame. Furthermore, great care was taken to secure pure hydrogen for sputtering and the slightest air leak always meant a ruined film.

The fact that there was apparently an escape of hydrogen during the heating process is not taken to have any particular significance. It is true

[7] Speed and Elmen, Trans. Am. Inst. Elect. Engineers, **40**, 1321 (1921).

that occluded hydrogen modifies[8] somewhat fundamentally the magnetic characteristics of some metals. But it is hard to see how this fact can be used to explain the non-magnetic character of these nickel films, when, as already stated, thicker ones, or, for that matter, films deposited with an induction coil, may turn out strongly magnetic.

The absence of Hall effect in the unheated films is not unreasonable in view of their amorphous character. The fact that they show no magneto-optic rotation, however, is probably a purely magnetic phenomenon and due to the lack of high internal magnetic fields in the non-magnetic specimen.

While no evaporated films have been tested as yet in connection with the present experiments, one of the writers found, a few years ago, that evaporated nickel films showed magneto-optic rotation. This doubtless means that such films are ordinarily magnetic[9] and therefore crystalline, as was found by Steinberg[10] to be the case for evaporated silver and iron.

In conclusion, the writers accept the common view of the sputtered film as an aggregate which is brought into a greater degree of coalescence by heating. As the present work shows, this aggregate may be initially amorphous in some cases, if temperature and voltage conditions during deposition are properly controlled. Whether the sputtered particles are single atoms, as assumed by some investigators, or actual granular crystals, as believed by Kahler,[11] is a much-discussed question on which this work perhaps throws a little light. For the amorphous film must be built up either of single atoms or of exceedingly small groups, while, on the other hand, the apparent effect of higher voltages in producing crystalline films would be in accord with the view of such voltages giving larger sputtered particles, crystalline in character—although, of course, there are other possible explanations, such as local heating accompanying the higher voltage.

Cobalt and iron films are now being investigated to see to what extent they bear out these conclusions for nickel, particularly as regards the connection between magnetization and crystal structure.

Acknowledgment is gratefully made to the Rumford and American Association funds for grants which have aided this research.

PHYSICAL LABORATORY,
UNIVERSITY OF WISCONSIN,
March 28, 1925.

[8] A. E. Oxley, Proc. Roy. Soc. **101,** 264 (1922).
[9] On this point see A. J. Sorensen, Phys. Rev. **24,** 658 (1924).
[10] J. C. Steinberg, Phys. Rev. **21,** 22 (1923).
[11] H. Kahler, Phys Rev. **18,** 216 (1921).

ON ELECTRIC CHARGES CARRIED BY INDIVIDUAL MICROSCOPIC PARTICLES*

By Th. Sexl

Abstract

Criticism of conclusions as to the existence of an elementary electronic charge, from experiments of Derieux with mercury droplets.—In these experiments observations of the same droplet were made at different pressures. The size of one droplet which apparently was constant in mass and not disturbed by air currents, is computed and a result obtained different from that obtained by Millikan's method of computation. The charges computed by using the size so determined are not multiples of a unit charge. This confirms Ehrenhaft's conclusion that other electric charges are stable on microscopic and submicroscopic metallic particles than those stable on particles of dielectrics.

(A reply by J. B. Derieux follows this article.—Ed.)

F. EHRENHAFT[1] and his pupils working with particles of precious metals (silver, platinum, gold and mercury) suspended in inert gases (N, Ar etc.), found on them electric charges down to 10^{-12} electrostatic units. This led him to the conclusion that the existence of an elementary charge is not yet proved by experiment.

R. A. Millikan[2] and his pupils on the other hand are of the opinion that they have succeeded in proving that all static charges both on insulators, such as oil (Millikan) and shellac (Lee[3]), and on conductors, e. g. mercury (Derieux[4]) are built up of elementary charges.

Two very strong objections, however, may be urged against the method used by R. A. Millikan and his pupils. The first is that all measurements are made on big droplets, their radii being always greater than 3×10^{-5} cm. The second is that these authors a priori presuppose an equality of charges on all test particles, i.e. the existence of an elementary charge, in determining the size of the charged particles, which is

* Contrary to the general editorial policy of the Physical Review, this criticism is published in spite of the fact that it is believed to be erroneous, because of the importance of the subject, and because it was submitted by Professor F. Ehrenhaft. A reply by J. B. Derieux and a discussion by R. A. Millikan follow this criticism.—G. S. F.

[1] F. Ehrenhaft, Anz. Wiener Akademie, March 4, 1909; April 21, 1910; May 12, 1910; Wien. Ber. **119**, 882 (1910); Phys. Zeits. **11**, 940 (1910); Ann. der Phys. **44**, 657 (1914); **56**, 1, (1918); **63**, 773 (1920).

[2] R. A. Millikan, Phys. Zeits. **11**, 1097 (1910); Phys. Rev. **32**, 349 (1911); Phys. Zeits. **14**, 736 (1913); Phil. Mag. **34**, 1 (1917).

[3] I. Y. Lee, Phys. Rev. **4**, 420 (1914).

[4] J. B. Derieux, Phys. Rev. **11**, 203 (1918).

the essential element of the droplet method. In the following a method will be put forward by which the radius of a particle is determined without any assumption of the existence of an elementary charge.

The Stokes-Cunningham law of motion

$$(4/3)a^3\pi(\sigma-\rho)g=6\pi\mu a v_f(1+Al/a)^{-1}$$

can be written in the form $\alpha+\beta l=v_f$ if $(2/9)(\sigma-\rho)ga^2/\mu\equiv\alpha$ and $(2/9)(\sigma-\rho)gaA/\mu\equiv\beta$. It postulates a linear relationship between v_f and l. Since it is possible to measure the speed of fall of the same particle at various gas-pressures[5] the individual straight line is fixed by means of $\alpha=(v_1l_2-v_2l_1)/(l_2-l_1)$ and $\beta=(v_2-v_1)/(l_2-l_1)$, which quantities can be determined experimentally. If all assumptions hold[6], we can compute the radius of the particle from the equation

$$a=\sqrt{(9/2)\mu\alpha/(\sigma-\rho)g}.$$

This method of determining the size of the carrier of the electric charge is independent of every assumption about its charge.[7]

Now a pupil of R. A. Millikan, J. B. Derieux, has succeeded in measuring the same mercury droplet at varying gas pressures. But he did not use the above-mentioned method of calculating the radius of the droplet without recourse to assumptions about an elementary charge. Therefore by calculating the radii also according to this method, it is possible to examine R. A. Millikan's method which was used by J. B. Derieux for the determination of the radii of his particles.

On considering the data given by Derieux we find at first sight the astonishing fact that among eleven mercury-droplets (record numbers 51-61) which could be measured at varying gas-pressures, there are three for which the times of fall are longer at reduced pressures than at atmospheric pressure. Such a behavior seems at first to be unintelligible. For a more detailed discussion we plotted the reciprocals of the times of fall (speeds of fall, since distance of fall is 1 cm) as ordinates against the mean free paths l as abscissas. Through every pair of points belonging to one particle straight lines were drawn. The diagrams thus found are analogous to those already given by R. Baer.[8] Subsequently the radius and the density of these particles were computed according to the method used by R. Baer. For this computation the value of the constant

[5] First stated by E. Meyer and W. Gerlach, Ann. der Phys. **47**, 224 (1915) and I. Parankiewicz, Phys. Zeits. **19**, 280 (1918).

[6] (a) Sphericity of the test particles; (b) validity of the Stokes-Cunningham law with a constant A; (c) density of the particles equal to that of the material in bulk.

[7] Compare Zeits. f. Phys. **16**, 34 (1923).

[8] R. Baer, Ann. der Phys. **59**, 394-403 (1919).

$A = 0.708$, given by R. A. Millikan for mercury-air, was assumed. The following values were found

Drop No. :	53	55	56	57	58	59	60	61
$a(10^{-5}$ cm) :	72.73	15.59	24.37	14.44	5.149	5.805	4.213	5.051
σ(g cm^{-3}) :	1.233	1.718	0.961	2.623	11.19	9.719	20.54	19.53

In analogy to R. Baer's criticism[8] of Ehrenhaft's results, it would seem possible to conclude that the mercury-droplets observed by Derieux and used as evidence for the existence of an elementary charge by R. A. Millikan are either non-spherical or are of spongy structure. Such a conclusion is, however, absurd since the particles were produced by condensing the vapor of boiling mercury. We therefore must try to find a more plausible explanation for this curious behavior. Now the air in the condenser was pumped off through six holes in the center of the upper plate only, so it could happen that equilibrium between the air in the condenser and the air in the pressure-cylinder[9] was not reached when the time-measurements began. Therefore a rising current of air could have remained in the condenser. The result of this would be that the observed values of v_f would be found too low. Since an approximately constant current in the condenser would not influence the values of v_1+v_s,[10] these values were plotted as ordinates against the mean free paths l as abscissas. It appeared that all the straight lines which were drawn through related points showed a uniform upward direction, with a few curves crossing the others. The reason for this could not be found, because the particles are not recorded in detail (detailed records are given only for droplets No. 59 and 60).[11]

The criterion for proving the absence of a current or another disturbance of the measurements is to be found in the constancy of the balancing-potential[12] which can be computed separately for the different pressures (from the equation $f^* = ([v_f/(v_f+v_s)]f)$. The detailed recorded measurements of the droplets No. 59 and 60 were examined with regard to this condition. We find

Drop No.:	59			60			
Pressure in mm Hg:	750.9	348.1	196.3	751.0	430.7	299.5	180.0
f^*:[13]	3.346	3.128	3.016	4.702	4.731	4.721	4.672

[9] Compare J. B. Derieux, l.c.[4] p. 205.

[10] Computed from the recorded radii of the particles by means of the equation $(4/3)a^3\pi(\sigma-\rho)g = ef^*$.

[11] Perhaps the evaporation of the droplets which according to J. B. Derieux is greater at reduced pressures accounts for the deviation.

[12] R. Baer, Ann. der Phys. **67**, 182, 1922. By balancing-potential that potential is understood at which the weight of the drop is balanced by the electric field. The above-mentioned formula follows from the equations $ef^* = mg$, $mg = v_f/B$ and $ef - mg = v_s/B$ (f = field-strength in the condenser.)

[13] Computed for the charge which Derieux considers as built up of four elementary charges.

For droplet No. 59 there results a maximum fluctuation of ten percent against only one percent for droplet No. 60. If we compute the mean errors of the balancing-potentials in the usual way we find an error of one percent at most. Consequently, the fluctuations for droplet No. 59 fall beyond the limits of error, which means the presence of a disturbance (current in the condenser, inconstancy of the mass of the droplet caused by gradual evaporation etc.). On the other hand, the fluctuations of the balancing-potential for droplet No. 60 lie within the limits of error and therefore the measurements can be taken as free from disturbances (no current in the condenser, constancy of the mass of the particle). Having thus gained an opinion about the trustworthiness of the measurements we can determine the size of these droplets.

By plotting their times of fall as ordinates against the mean free paths as abscissas it is shown that the linear relationship between v_f and l postulated by the Stokes-Cunningham law exists indeed. Therefore a and β belonging to each of the straight lines were computed by means of the method of least squares. It is seen from the equation $ef-mg=6\pi\mu a v_s(1+Al/a)^{-1}$ or $a'+\beta' l=v_s$, that a linear relation must also exist between v_s and l. It should be $\beta'/a'=\beta/a=A/a=c$. a' and β' were computed in the same way as a and β. But the batteries ran down and a little current might after all have been in the condenser. To eliminate these small sources of error a'' and β'' belonging to the values of $(v_f+v_s)/f$, not touched by these sources of error, were computed by means of the method of least squares. It was found[14]

	v_f	v_s	$(v_f+v_s)/f$	v_f	v_s	$(v_f+v_s)/f$
Drop No. :	59			60		
$(\beta/a)10^{-3}$:	147.3	239.6	220.4	165.1	167.9	171.2
$a\times10^5$:	4.794	4.481	4.671	5.196	5.184	5.169
$e\times10^{10}$:	4.588	3.962	4.243	4.156	4.124	4.091
A :	0.706	1.074	1.029	0.858	0.871	0.885
a(Derieux) :			4.815	5.445		
A(Derieux) :			0.832	0.803		

The non-agreement of the values of β/a gained for droplet No. 59 shows once more the presence of a source of error, as already inferred from the inconsistency of the balancing-potential.[15] The fluctuations of the values of β/a for droplet No. 60, however, lie within the limits of error,

[14] It should be mentioned that the electric charges measured on these big droplets are as follows: particle No. 59: 8.471; 12.717; 16.970.$\times10^{-10}$; particle No. 60: 12.310; 16.624; 20.795; 25.110$\times10^{-10}$ electrostatic units. The exact multiples of the electronic charge would be: 9.548; 14.322; 19.096; 23.870; 28.644$\times10^{-10}$ electrostatic units.

[15] Nevertheless, the radius computed from the values of $(v_f+v_s)/f$ cannot be in error of more than one percent under the assumption that it is essentially a current that produces the disturbance of the measurements.

as it can be shown, and the radius computed from the values of v_f cannot be in error by more than one half percent.

Thus we find that the radii of the droplets computed by us by means of a method free from assumptions about an elementary charge, and the radii computed by Derieux according to the method of R. A. Millikan from the equation $mg = ef^*$ differ by more than four percent. Therefore the electric charges carried by these mercury-droplets show deviations of more than 14 percent[16] from the electronic charge and its multiples.

These deviations are in agreement with those observed by Ishida[17] on oil-drops and Silvey[18] on mercury-droplets.

To sum up it could be shown that all the measurements taken by Derieux at different gas-pressures were disturbed by causes that, however, could not be found, because the particles are not recorded in detail. Only the measurements taken on particle No. 60 could be shown to be free from these disturbances (no current in the condenser, no evaporation of the droplet). Therefore a value for the constant A could be computed from the measurements on this particle. The value of the constant A was found to be 0.858 against the value 0.708 given by Millikan. The sphericity of the particles being beyond doubt, the only assumption for this computation is that the density of the particle is equal to that of the material in bulk. On the other hand the assumption of a constant $A = 0.708$ would mean a density of this mercury droplet $\sigma = 21.2$.

As it is well-known, R. A. Millikan always brought forward the paper of J. B. Derieux as a proof[19] for the theory that all electric charges carried by mercury-droplets are of the same value (4.774×10^{-10} e.s.u.) as those carried by insulators. The present investigation shows the fallacy of this argument.

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July 14, 1924.

[16] At least ten percent of this lies beyond the limits of error.
[17] Y. Ishida, Phys. Rev. **21**, 561 (1923).
[18] O. W. Silvey, Phys. Rev. **7**, 102 (1916).
[19] R. A. Millikan, Phys. Rev. **8**, 620 (1916); "The Electron," p. 176, 1917.

REPLY TO TH. SEXL'S CRITICISM OF R. A. MILLIKAN'S METHOD OF COMPUTATION OF THE ELEMENTARY ELECTRICAL CHARGE ON MERCURY DROPLETS

By J. B. Derieux

Abstract

It is shown that Sexl's test method is in error because it is based upon the assumption that the droplets remain of the same size throughout the observations. Data are given which prove that because of evaporation such is not the case. Errors, also, are shown in his computations, which, when corrected give results approximating those by the Millikan method, with the difference in favor of the Millikan method.

THE method suggested by Th. Sexl[1] for testing Millikan's method of computing the elementary electrical charge, by using the writer's results[2] at varying pressures, assumes that the radius of a droplet remains constant through varying pressures. That this is certainly not true, is beautifully demonstrated by the three droplets which Sexl discarded as being unintelligible. They had evaporated so much by the time the observations at reduced pressure were reached that their times of fall under gravity were less than at atmospheric pressure. These droplets showed excessive rates of evaporation at atmospheric pressure, and this continued at reduced pressure. Therefore it is most certain that the evaporation did not cease during the intervening period, and then start again. Number 52 was the most striking one. Its mean times of fall at atmospheric and reduced pressures were 12.54 and 18.44 sec., respectively. At atmospheric pressure it started at 12.10 sec. and evaporated to 13.36 sec.; at reduced pressure it was reduced from 17.60 to 19.20 sec. The periods of observation were about 20 and 15 min., respectively, while the intervening period was considerably longer than either, for I evacuated very gently so as not to disturb the remaining air very much, and then I waited until I was confident that any air currents had ceased. Therefore it cannot be doubted that the increase in time of fall at reduced pressure over that at atmospheric pressure is the result of evaporation during the intervening period. The other two droplets present similar evidence.

With these three droplets most certainly demonstrating the smaller size at reduced pressure, it is evident that it is erroneous to assume no change. No droplet can be treated as the same droplet at two pressures, but must at each pressure be considered as a separate and distinct one. This is just what I did in all the work which is here under discussion, as may be seen from my original paper[2] in which I not only stated this fact

[1] Th. Sexl, preceding paper.

[2] J. B. Derieux, Phys. Rev. **11**, 203 (1918)

clearly but recorded different radii for all my drops at different pressures. With No. 52, just referred to, for example, I recorded its radii as 6.604×10^{-5} cm at atmospheric pressure, and 5.163 at reduced pressure. And yet Sexl deliberately ignores all this and assumes the same radius for all pressures. Hence, obviously, the error of his results.

However, I did not understand why the results by his method should be as much in error as his published values, and so I computed the radii by his method, taking

$$a^2 = 9\mu(v_1 l_2 - v_2 l_1)/2(\sigma - \rho)(l_2 - l_1).$$

It was expected that the results by his method would be too large, for evaporation had so reduced the sizes of the droplets that v_2 was too small. Below are the results of my computation by Sexl's method given in comparison with those by Millikan's method. It is evident that Sexl had made inexplicable errors in his computations or has used incorrect values of his constants for his results do not agree with the ones which I obtain by his method.

Drop number:	53	55	56	57	58	59	60	61
By Sexl's method (my calc.):	6.98	5.51	6.36	6.39	4.68	4.83	5.23	6.03
By Millikan's method:	6.83	5.38	6.15	6.12	4.76	4.81	5.38*	6.07

They agree as well as could be expected, and the difference is in favor of Millikan's method, which gives the smaller value, as predicted, for the droplets which show reduction in size by evaporation. His values for Nos. 58, 60, and 61 are larger than those by the other method, which appears unfavorable at first thought, but these droplets show an increase in size during observation, and, consequently, Sexl's method would give values too small for them.[3]

The balancing potentials, contrary to his statement, are not constant, but show a decided decrease in droplets which show a reduction in size, as may be noticed from his values—3.346, 3.128, and 3.016—for No. 59. This gives further evidence of a reduction in size of the droplets.

The fact that the fluctuations in the results from No. 59 are greater than those from No. 60, which fact Sexl makes use of, is easily to be accounted for by evaporation of No. 59.

The conclusion is that Sexl's criticism of Millikan's method has no foundation, being based upon a wrong assumption.

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February 1925.

* In the original paper, by an error in calculation, 5.44 was given instead of 5.38, and on p. 222, by typographical error, 5.29 was given for 5.39.

[3] J. B. Derieux, l.c.,[2] pp. 223-224.

THE NATURE OF THE EVIDENCE FOR THE DIVISIBILITY OF THE ELECTRON

By R. A. Millikan

Abstract

The purpose of this note is to remove misconceptions due to erroneous statements regarding the determination of the elementary electronic charge by the oil-drop method. It is emphasized that the existence of an elemental charge is directly proved by the multiple relationship shown to exist between successive charges on each test particle; that the unitary character of electricity is not presupposed even in determining the absolute value; and that the method used by Sexl in determining the radius of the droplet is not essentially new. Recent photo-electric work of Hake and of Wasser is discussed briefly.

FOR the past eight years I have taken no part in the discussion of the nature of the evidence for the divisibility of the electron, since it has seemed to me that the published data told the story quite plainly to any one who would take the trouble to examine them critically. Further, I stated the case as clearly as I could in 1916[1] and no evidence has appeared since to modify the conclusions then drawn, or, indeed even to need further discussion, save only the very recent photo-electric work of Hake[2] and of Wasser,[3] which will be touched upon below.

I believe that every one of the observers outside of Vienna who has repeated my work has both checked my experimental results and reasserted my conclusions upon all the essential points in dispute,[4] while even in Professor Ehrenhaft's laboratory itself one observer, Schmid,[5] has found, like all the rest of us, that measurements upon the Brownian movements of minute suspended particles in air do not lead, as formerly asserted in Vienna, to too low a value of Ne, while another observer, Mattuck,[6] has found by using my oil-drop method without any essential modification, that my results, both as to the complete law of fall of a spherical particle and as to the uniform appearance upon all particles, little and big, of the charge of about 4.7×10^{-10} electrostatic units, were correct within the limits of his rather large experimental error.

[1] Millikan, Phys. Rev. **8**, 595-625 (1916).
[2] Hake, Zeits. f. Phys. **15**, 110 (1923).
[3] Wasser, Zeits. f. Phys. **27**, 226 (1924).
[4] See Bär, Ann. der Phys. **67**, 157 (1922); also Die Naturwissenschaften **14** and **15**, 1922.
[5] Schmid, Zeits. f. Phys. **5**, 31 (1921).
[6] Mattuck, Phys. Zeits. Dec. 1, 1924, p. 620.

Scarcely any further extensive discussion of the sub-electron problem then seems necessary now, but it is perhaps worth while to correct, for the benefit of those who have not the time to study the original data, some fundamental misconceptions which may have been gained from erroneous statements which have been repeatedly made in the course of this discussion and which are reasserted by Sexl.

1. *Nothing could be more fundamentally incorrect than the statement that my method presupposes an equality of charge on all test particles, i. e., the existence of an elemental charge.* It is altogether obvious that no assumption whatever regarding the character of the charge e on the droplet is involved in my fundamental equation

$$\frac{v_1}{v_2} = \frac{mg}{Fe - mg}$$

or

$$e = (mg/Fv_1)(v_1+v_2) = K(v_1+v_2).$$

This equation shows that the charge e on the drop, whatever its value, is proportional to the velocity communicated to the drop, namely (v_1+v_2) by the constant field F acting on the charge e. In other words, this charge e is measured in my method in terms of the speed (v_1+v_2). The essence of the method consists in *changing* the charge and hence v_2 by capturing ions, by photo-electric discharge, by x-rays, α, β and γ rays, etc., and in finding by such change all the values of (v_1+v_2) that can be obtained. The atomic nature of electricity is revealed conclusively in the experimental fact that this series of possible speeds is actually found to bear the relations 1, 2, 3, 4, 5. *It is in this purely experimental multiple relationship in the speeds of drops all of which capture the same sort of ions from the air that the proof of the atomic theory of electricity rests, and it is at this point that the attack on the atomic theory of electricity must be made if it is to be worthy of any serious consideration whatever.*

Now, so far as I know, no one has ever published any data that are susceptible of careful analysis for this multiple relationship and that yet fail to reveal it. Further, no data should be considered as evidence in which the charge upon a given drop is not changed enough times to test thoroughly the existence or non-existence of this multiple relationship. In so far as I can see from the rather meager data that Hake and Wasser publish in their recent photo-electric work, their drops do show this unitary progression of charge, and if they do then it may be taken as practically certain that these gentlemen are not dealing with sub-electrons, for I have demonstrated conclusively that the charges caught from ionized air, such as some of the observed charges will always be if

the observations are long continued, are uniformally electrons, and I think it is not too much to assert that they must be electrons in Vienna if they are such in Pasadena and Chicago.

It is true that I do not yet understand fully what Wasser calls his "inverse photo-electric effect," but it seems to me likely that he obtains this effect by catching electrons released from the surrounding walls by ultraviolet light instead of by detaching positive charges from his droplet by ultraviolet light, as he thinks that he does. But this point can be tested easily, and we are in the process of making this test in this laboratory. By changing the charge on a given drop, first with the aid of ultraviolet light and then by throwing upon it ions produced by the passage of a beam of x-rays underneath the drop, it will be possible to observe directly whether these two changes in charge produce the same change in speed. The question of the appearance of the sub-electron in these experiments can then be settled definitely without making any assumptions whatsoever about the densities of the drops worked with.

2. *It is fundamentally erroneous to suppose that even in the reduction of the value of the electron from velocity units to absolute electrostatic units—an operation which does presuppose the density and sphericity of the droplet—any presupposition whatever as to the unitary character of electricity is involved.* A glance at any of my early papers upon this subject will show that the radius a of the drop was determined entirely from Stokes' law—or from a slightly corrected form of Stokes' law—and involves no suppositions of any kind as to the nature of the electrical charge. The two-thirds' power of the smallest charge (measured in terms of a speed) *that the drop actually carried*—this smallest charge could be unerringly computed from the observed multiple relationship in speeds, but not even this computation was necessary since plenty of drops could be obtained upon which it was *directly observed*—was plotted against $1/pa$, a being computed from Stokes' law, viz: $mg = 6\pi\mu a v_1$. This plotting yielded a single straight line. It is quite true that it could not have done this unless all of the drops, when most lightly charged, carried one and the same unit charge, as the multiple relationship had already shown that they did, *but the straight line, like the multiple relationship, is an experimental fact* from which the unitary character of the charge follows. *It is not an assumption.* The absolute value, too, of the electron was now approximately determined by the intercept of the straight line on the $e_1^{2/3}$ axis. This line also yielded, through its slope, the approximately correct value of the first correction term, A, to Stokes' law, which thus became $mg = 6\pi\mu a v_1(1+Al/a)^{-1}$. This new equation, with A now approximately known, was then solved to obtain a final value for a for use in the more

exact computation of e. All this was carefully explained in all my early papers.[7] It is true that in my later papers,[8] after the existence of the electron had been demonstrated and its value accurately determined, I found it in the interests of both convenience and accuracy to use the the value of e for working back to a, and this I often did, but it was in no way essential to my method and was actually never used until the value of e had been accurately found without it. *In other words, my method of determining the size of the carrier of the electric charge is in fact completely independent of every assumption about the value of this charge.*

3. It is fundamentally erroneous to suppose that the method used by several observers, including Sexl, of determining the radius of the drop by assuming its sphericity and density and then measuring its speed of fall at two different pressures is in any important respect an *essential* modification of my method, for *there is no relationship here involved that is not included in my linear relationship between* $e_1^{2/3}$ *and* l/a, *or* $1/pa$. I exhibited my results in this single-line form because it is by far the most comprehensive and by far the most elegant mode of treatment of oil-drop data. It is simply Stokes' law, with a first correction term added, that requires the linear relation between v_1 and l, mentioned by Sexl, and it is the same law plus the unitary character of electricity out of which grows the linear relation between $e_1^{2/3}$ and l/a. The straight line between v and l is a different one for each drop because the drop-radius has not yet been eliminated from it. By its elimination in the $e_1^{2/3}$, l/a line all of these v, l lines have been reduced to a single one, as is beautifully shown in my published data.

Again, after I had changed both pressure (l) and drop-radius a and found that 99 percent of my drops fell upon the single $e^{2/3}$, l/a line it obviously became superfluous to change l alone as these other observers do, for if a point cannot get off the line by varying at random both l and a it clearly cannot do so by varying l alone and holding a constant.

Further, the reason that in my early experiments I did not change l alone in this way—an operation which takes a relatively long interval of time—was that on account of the slow change in size of all drops, especially of mercury drops, this method was less accurate than the one I did use of changing both l and a and thus getting a group of velocity-measurements close together in time and hence practically free from evaporation errors. If an occasional one of my points fell entirely off this line it meant, as I pointed out fifteen years ago, simply that this

[7] Millikan, Phys. Rev. (1) **32**, 379 (1911)
[8] Millikan, Phil. Mag. **34**, 3 (1917)

drop had not the assumed density or sphericity. It might, indeed, conceivably have meant, had the observation stood by itself, that the charge carried was a fraction of an electron while the assumed density and sphericity were correct. This was the way Ehrenhaft chose to interpret his irregularities, *but this alternative was barred out by the observed multiple relationship in speeds* and also by the fact that *Ne* when computed from Brownian movements came out as in electrolysis.[9] It became possible at once in the case of a drop that fell off my line, to obtain the correct equivalent density of a spherical drop by inserting such a density-value as would make the drop fall on that line. This is precisely what I did as early as 1911, and it is essentially what these other more recent observers, including Sexl, do when they work back to density or drop-radius from their v, l line, except that they ignore evaporation and in the case of mercury at least introduce large errors thereby.

It is true that Meyer and Gerlach[10] and Bär[11] performed an important service by computing the densities of particles produced by Ehrenhaft's method from the linear v, l relation instead of the linear $e_1^{2/3}, l/a$ relation, such as I used, for though the two methods, in view of my multiple relationships, must yield the same results, barring evaporation, Meyer and Bär's result is, as they point out, entirely independent of the existence upon their particles of any charge at all, so that when they find by their procedure, as I had done from mine, that Ehrenhaft's assumed densities are entirely wrong they remove from him the possibility of calling upon any electrical assumption whatever, for explaining his irregularities. In other words, Meyer and Bär added a third demonstration, independent of the two that I used as mentioned above, that Ehrenhaft's irregularities are due to the assumption of incorrect drop densities. It may be added, too, that there is no apriori reason why some of Hake and Wasser's droplets may not be made up of clusters of particles of little more than molecular dimensions even though they are formed from the condensation of pure mercury, and such clusters may conceivably have a different long wave-length limit from that of mercury in mass. For it will be remembered that it requires light of wave-length about 1200 angstroms to detach electrons from mercury molecules, while the long wave-length limit of liquid mercury is 2635 angstroms. This point, however, will be settled by experiments now in progress.

In Derieux's work upon mercury, it was found impossible—as he clearly stated—to prevent evaporation, but by taking a series of consecutive

[9] Millikan, Phys. Rev. **8,** pp. 610-11 (1916).
[10] Meyer and Gerlach, Ann. d. Phys., **47,** 227, 1915.
[11] Bär, Ann. der Phys. **59,** 393 (1919) and Ann. der Phys. **67,** 157 (1922).

observations in rapid succession he was able to render its influence small and he then found, by assuming his drops spherical and of density 13.56, that all of his points fell close to a straight line of slope $A = .708$ and having an intercept at the correct value for the electron. It then follows, as a matter of necessity, that if there had been no evaporation, and if the points had all been exactly on the .708 line, Sexl could not get by using Bär's method of computing drop-radius and density as he does (working back from the observed v, l line) different values of a and σ from those used by Derieux, unless one or the other of them made numerical blunders. It is not important to search for such blunders since Sexl's critique of Derieux's results is completely without significance because of his astonishing disregard of evaporation in spite of Derieux's full discussion of it.

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February 24, 1925.

ON ELSTER AND GEITEL'S THEORY OF THE ELECTRIFICATION OF RAIN DROPS

By T. E. W. Schumann

Abstract

Electrification of large drops by collision with small drops in an electric field.—The following experiments were made to test *Elster and Geitel's theory of the electrification of rain drops.* Large drops (A drops) falling between the horizontal parallel plates of a charged condenser, were sprayed from below with a fine stream of small drops (B drops) and the charge on the A drops was found to be of the same sign as that of the upper plate and to be proportional to the field strength. From the charge per A drop and the probable number of collisions with B drops, the charge per collision was computed and found to be zero for B drops of radius less than 0.18 mm and then to increase rapidly with the radius to 0.4 mm. Photographs taken with a motion picture camera show that the B drop first coalesces with the A drop and then, if its momentum is sufficient, a protuberence is produced on the upper surface of the A drop, which breaks up into a number of small droplets which carry off with them not only part of the A drop but also some charge. Very small B drops probably merely coalesce with A drops. In the case of falling rain, cloud droplets are too small to have a charging effect, and the effect of larger drops overtaking smaller ones is to weaken the existing field. Hence it is doubtful whether this phenomenon alone can explain the observed charges on raindrops and it certainly does not explain such high potential differences as occur in lightning discharges.

ELSTER and Geitel[1] proposed two theories to explain the electrical charge on rain, snow, etc. Geitel[2] gives a resumé of the second theory in the following way.

"Consider a falling drop of water in the normal electric field of the earth. The drop would be electrically polarized, the lower surface being positively charged, the upper surface taking on a negative charge. On its way to the earth it encounters a smaller drop whose terminal velocity is therefore less. When the smaller recoils from the lower surface of the larger, it takes along some positive charge, which is carried up along with it by the ascending air-currents. It is clear that the collision of the drops in this way would cause a *strengthening* of the existing field, the free charges (positive and negative) being carried against the lines of force. . . . . And so there is a possibility that the existing field may be increased to such an extent that discharges (in the form of lightning) may at last take place."

[1] Elster and Geitel, Phys. Zeits. **14,** 1287 (1913).
[2] H. Geitel, Phys. Zeits. **17,** 455 (1916).

For the sake of brevity we shall in future refer to the large drops as A drops, and to the small ones as B drops.

In the older theory of Elster and Geitel, afterwards discarded by them, it was assumed that the B drops moved in the streamlines around an A drop, the last point of contact between the drops being on the upper surface of the A drop. In this case the electrical action is directly the opposite of that described above, i.e., the tendency is to weaken the existing field. The object of this work was to test these two theories experimentally.

Description of the Apparatus

Large drops of water (A drops) are allowed to fall into a small vessel which is connected to a quadrant electrometer so that the charge on an A drop may be accurately measured. These drops fall through two holes cut centrally in the plates of a parallel-plate condenser mounted so that the gradient of the field is vertical.

A fine stream of B drops issues from a small orifice and is shot from below through two narrow slits cut in the condenser plates, so that it meets the falling A drops halfway between the plates, i.e. in an electric field of known and variable intensity. The customary insulating and shielding precautions are taken so that both the A and the B drops are initially uncharged. That this is the case can be further verified by measuring a charge on the A drops in a zero field. This was done and no charge was found.

Experimental Results

As soon as an electric field was established the A drops showed a charge, caused by coming in contact with the B drops. The strength of the field was varied, and it was found that the charge was directly proportional to the field-strength when measured for a great number of drops, since the charge on a single drop is subject to probability fluctuations. The sign of the charge is in the sense of Elster and Geitel's first theory—in a normal field (top plate positive) the A drops are positively charged. It was therefore assumed that the B drops in some way travel around a falling A drop, and that contact is last made on the upper surface of the A drop.

The next step was to make quantitative measurements of the magnitude of the charge for a single collision. To do this the following determinations have to be made.

(a) The charge on an A drop could easily be determined, as remarked above, by measuring the charge on a counted number of A drops by

means of the quadrant electrometer, whose constants are readily measurable.

(b) The other quantity to be determined is n, the average number of B drops colliding with the A drop in any particular experiment. To determine n we measure the respective sizes of the A and B drops, their respective velocities at the point of collision, and the weight of B drops passing per second. Knowing these the calculation of n is a mathematical problem,[3] and the average charge e produced by a single encounter is got by dividing the charge of the A drop by n.

To fix our ideas and to get a measure of the extent to which charging takes place, we introduce the following considerations. The maximum charge which a small sphere can obtain by contact with a large electrically neutral sphere which is polarized by a uniform electric field of intensity F, is given by the expression[4] $\frac{1}{2}\pi^2 \cdot Fr^2$ where r is the radius of the small sphere. Although this represents a highly idealized case, and would not at all apply rigidly to our A and B drops, which naturally change their shape, and even coalesce, as we shall see later on, yet we can use this expression quite conveniently to define the extent to which charging takes place. Let

$$k = 2e/n\pi^2 Fr^2$$

Then k is the ratio of the experimental charge on a B drop to this maximum theoretical charge, and is a measure of the electrical action.

It was found that the value of k depends mainly on the size of the B drops, a variation in the size of the A drops making very little difference, provided they remained fairly large compared with the B drops. The relative velocities employed were of the order of the difference between the terminal velocities of the A and B drops when falling freely in air at atmospheric pressure. Small variations in this relative velocity did not seem to affect the value of k to any appreciable extent. However, it is probable that the relative velocity plays a very important part: for a certain size of B drop a small variation in the relative velocity may very likely cause quite a large variation in k. This point, however, was not carefully investigated, because at the time when these experiments were performed the mechanism of collision, as revealed by photographs taken at a much later date, was not fully understood. A table follows giving the value of k for different sizes of B drops.

Radius of B drops	k
0.363 mm	0.77
0.250	0.61
0.185	0.075
0.179	0.013
0.148	−0.002

[3] For complete details see T. Schumann, Göttingen Dissertation 1924.

[4] Poisson, Mem. de l'Inst. (1811) p. 196.

To explain the values thus obtained it was at first assumed that in some way or other the B drops go *around* the A drops, the last point of contact between two drops being on the upper surface of the A drop. The larger the B drop the further it goes around, and the last point of contact is therefore in a region where the surface density on the A drop has a high value. When the radius of the B drop r is reduced to about 0.18 mm it goes no further than the horizontal equator of the A drop. Here the surface density is zero and hence the B drop remains uncharged. As it was found impossible to produce uncharged B drops of a size smaller than 0.15 mm radius it was attempted to extend the table on theoretical grounds.[5] Making certain simplifying assumptions concerning the elastic impact between the drops, and taking into account the tendency of very small B drops to be carried in the streamlines of the air around a falling A drop, it was calculated that k would reach a *minimum* value of about -0.4 when r has the value of 0.03 mm, and tends towards zero when r becomes zero. A negative value of k means that the effect is reversed, i.e., the action would be in accord with Elster and Geitel's second theory, where it was supposed that the tendency is to strengthen the existing field. The above work was carried out at Göttingen, Germany.

It was felt, however, that the supposed motion of the B drops *around* the A drops was rather remarkable. Furthermore, the assumption that electrical contact between two drops is possible without their coalescing, hardly seems plausible. It was therefore decided to get photographic evidence of the manner in which drops of different sizes actually do behave when colliding. This part of the work was done at Yale University. As before, large drops fell through a stream of ascending B drops, and a rapid cinemetographic record was obtained of their motion.

Fig. 1 gives an example of many similar photographs obtained. Starting from the top right-hand corner and ending at the bottom left-hand corner, the downward motion of several large drops may be followed until after collision with the upward-moving small drops. As the photographs show, the drops first coalesce, but the momentum of the small drop carries it on, and produces a protuberance on the upper surface of the A drop, and this protuberance breaks up into a number of small drops. A small part of the large drop is thus actually *torn off* from its upper surface. This curious action completely explains the experimental results contained in the table given above. The small drops, breaking off at the top, carry along a negative charge with them (the field being normal), and the large drops convey a corresponding positive charge down to

[5] T. Schumann loc. cit.[3]

earth. Furthermore, it is highly probable that when the B drops are below a certain size, say 0.18 mm radius, their momentum would be too small to accomplish this tearing-off, and they would simply coalesce with the large drops. From this it is clear that the electrical action would not only depend upon the size of the B drops, but also on their relative velocity with respect to the A drops. Unfortunately in these experiments sufficient account was not taken of this fact. To approximate to the condi-

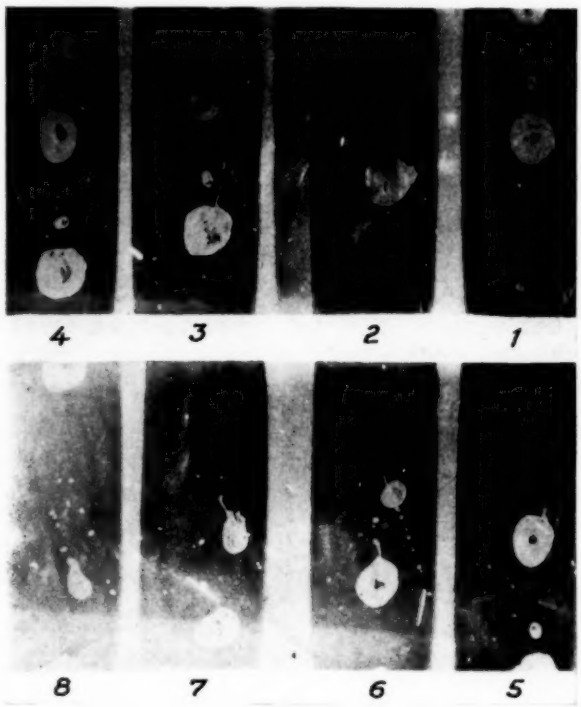

Fig. 1. Photos obtained with a motion picture camera, showing B drops passing through an A drop

tions in nature the relative velocity of a B drop with respect to an A drop should equal the difference of their terminal velocities falling in air of about atmospheric pressure.

Conclusion

Taking account of the experimental results obtained, we are inclined to believe that if the B drops have a radius below 0.18 mm they have no charging effect on larger drops, but probably coalesce with the large drops; or if they do rebound no electrical contact takes place and no

charging can result. The average radius of the drops that constitute the clouds is 0.01 mm so that as far as the action between cloud-drops and raindrops is concerned, Elster and Geitel's theory does not hold. If this is true, the theory loses its chief significance. For *raindrops* of different sizes, however, a modified form of their older theory does hold. Since this action has the tendency to weaken the existing field, their hypothesis about the production of potential differences between clouds and earth high enough to produce lightning must be discarded.

The only directly observable effect that we would expect, according to the results obtained, would be a weakening of the earth's field at the moment that the first raindrops begin to fall. The largest raindrops, having the greatest terminal velocity, would naturally reach the earth's surface first (unless they have to travel much further than the smaller drops), and if on their way they have come in contact with smaller raindrops, the charge would be such as to decrease the potential gradient. To get a more complete knowledge of the actual phenomena in nature it would be necessary to take simultaneous observations of the charges on rain and of the alterations in the potential gradient of the earth's electric field.

The author wishes to express his thanks to Prof. E. Wiechert, Director of the Geophysical Institute at Göttingen, who suggested this research, and to Prof. J. Zeleny of Yale, for his helpful interest in the latter part of the work.

Department of Physics,
Yale University,
December 23, 1924.

ON THE QUANTITATIVE THEORY OF ELECTROSTATIC SYSTEMS

By A. W. Simon

Abstract

General theory of cyclic electrostatic machines.—It is shown that if any system of insulated conductors is carried through a periodic cycle of electrostatic operations, the potential of any conductor of the system after n such cycles can be expressed in the form of a recurrent sequence. A general formula is then deduced for the potential of any conductor of the system after n cycles. The application of the formula to the case of electrostatic generators, electrostatic alternators, and electrostatic voltage multipliers is discussed. Methods of solution (1) for the case of a symmetrical alternator consisting of m inductors and m carriers so constructed that each carrier as it comes in front of an inductor is connected to the next following inductor, (2) for the Wimshurst alternator of four inductors and (3) for a new type of symmetrical alternator derived from the Wimshurst alternator by doubling the number of inductors. Finally it is shown how a simple electrostatic system can be made to function as a generator, alternator, or a voltage multiplier merely by a change of connections.

THE quantitative theory recently given for the influence electrostatic generator[1] can be immediately generalized to apply to any system of insulated conductors which are originally raised to various potentials and are then carried through a periodic cycle of electrostatic operations, if we define an electrostatic operation as (1) a moving about of the conductors of the system or (2) a making or breaking contact between any number of conductors of the system. If the system is under the action of only its own field, that is if none of the conductors are connected to sources of constant potential, then exactly the same reasoning given for the case of the influence electrostatic generator serves to establish the following general theorem:

If any electrostatic system is carried through a periodic cycle of electrostatic operations, the potential of any conductor of the system after n cycles satisfies an equation of the form

$$V_{n+m}+k_{m-1}V_{n+m-1}+k_{m-2}V_{n+m-2}+\cdots\cdots+k_0V_n=0 \qquad (1)$$

where the k's are functions only of the electric coefficients of the elements in certain configurations of the cycle, namely those in which a change of charge occurs on any of the elements.

[1] A. W. Simon, Proc. Nat. Acad. **10**, 302 (1924); Phys. Rev. **24**, 690 (1924).

Now Eq. (1) expresses the potential of an element in the form of a recurrent sequence, which can be evaluated by methods of the calculus of finite differences.

The solution[2] of (1) depends on the nature of the roots of the corresponding algebraic equation

$$r^m+k_{m-1}r^{m-1}+k_{m-2}r^{m-2}+\cdots\cdots+k_0=0 \tag{2}$$

If Eq. (2) has p pairs of imaginary roots of the form $\alpha_j \pm i\beta_j$, and consequently $(m-2p)$ real roots, none of which are repeated, then the general solution of (1) takes the form

$$V_n=\sum_{j=1}^{j=m-2p} C_j r_j^n+\sum_{j=1}^{j=p} \rho_j^n(C_{1,j}\cos n\theta_j+C_{2,j}\sin n\theta_j) \tag{3}$$

where the C's are arbitrary constants, r_j is a real root of (2), and θ_j and ρ_j are given respectively by $\tan\theta_j=\beta_j/\alpha_j$; $\rho_j=\sqrt{\alpha_j^2+\beta_j^2}$. Eq. (3) is the fundamental equation of all purely influence static machines. These may be divided into two classes: (1) Electrostatic generators (predominant roots real) as exemplified by machines of the Voss or Toepler Holtz type,[3] and (2) electrostatic alternators (predominant roots imaginary) as exemplified by a machine recently described.[4]

If next we examine systems in which some of the conductors are connected to sources of constant potential while the system is carried through its cycle, we find that for this case the potential of any conductor satisfies an equation of the form

$$V_{n+m}+k_{m-1}V_{n+m-1}+k_{m-2}V_{n+m-2}+\cdots\cdots+k_0V_n=K \tag{4}$$

where the small k's satisfy the same conditions as before, while K is a function of both the electric coefficients of the elements in certain configurations and of the constant voltages impressed on the system. Now the solution of (4) is the sum of the general solution of (4) with the second member equal to zero, i.e. a solution of the form (3), and a particular solution of (4). This particular solution is

$$V_n=K/(1+k_{m-1}+k_{m-2}+\cdots\cdots+k_0) \tag{5}$$

as can readily be verified.

Eqs. (3) and (5) together are the fundamental equations of a class of static machines known as electrostatic voltage multipliers, which have recently been described in detail elsewhere.[5]

[2] G. Boole, A Treatise on the Calculus of Finite Differences, Chap. XI.
[3] A. W. Simon, Phil. Mag. **49**, 257 (1925).
[4] A. W. Simon, Phys. Rev. **25**, 268 (March 1925).
[5] A. W. Simon, J. Opt. Soc. **9**, 345 (1924); also **10**, 669 (June 1925).

The solution of (1), as has been pointed out, depends on the possibility of finding the roots of Eq. (2), and while this cannot be done in every case, there are a number of special cases where this can be done readily, and these we shall now consider.

1. Symmetrical Electrostatic Alternators

These machines consist of m inductors and m carriers symmetrically mounted, and are so constructed that each carrier as it comes in front of an inductor is connected to the ith inductor following in the direction of rotation. The particular machine corresponding to $m=5$ and $i=1$, is shown in Fig. 1. If we set up the equations for such a machine, $(i=1)$, we find that the potentials of the nth and $(n+1)$st cycles are related by a system of equations of which the left members take the form:

$$\begin{array}{lllllllll}
aV_{1,n+1} & + & eV_{3,n+1} & + & dV_{5,n+1} & + & cV_{7,n+1} & + & bV_{9,n+1} \\
b & " & +a & " & +e & " & +d & " & +c \quad " \\
c & " & +b & " & +a & " & +e & " & +d \quad " \\
d & " & +c & " & +b & " & +a & " & +e \quad " \\
e & " & +d & " & +c & " & +b & " & +a \quad "
\end{array}$$

and the right members, similarly:

$$\begin{array}{lllllllll}
a'V_{1,n} & + & e'V_{3,n} & + & d'V_{5,n} & + & c'V_{7,n} & + & b'V_{9,n} \\
b' & " & +a' & " & +e' & " & +d' & " & +c' \quad " \\
c' & " & +b' & " & +a' & " & +e' & " & +d' \quad " \\
d' & " & +c' & " & +b' & " & +a' & " & +e' \quad " \\
e' & " & +d' & " & +c' & " & +b' & " & +a' \quad "
\end{array}$$

By the introduction of the symbolic operator r, which we define to be the same as the symbolic operator E of the calculus of finite differences,[6] we can write the above set of equations in the form

$$\begin{array}{lllllllll}
(ar-a')V_{1,n} & + & (er-e')V_{3,n} & + & (dr-d')V_{5,n} & + & (cr-c')V_{7,n} & + & (br-b')V_{9,n}=0 \\
(br-b') & " & +(ar-a') & " & +(er-e') & " & +(dr-d') & " & +(cr-c') \quad " \quad =0 \\
(cr-c') & " & +(br-b') & " & +(ar-a') & " & +(er-e') & " & +(dr-d') \quad " \quad =0 \\
(dr-d') & " & +(cr-c') & " & +(br-b') & " & +(ar-a') & " & +(er-e') \quad " \quad =0 \\
(er-e') & " & +(dr-d') & " & +(cr-c') & " & +(br-b') & " & +(ar-a') \quad " \quad =0
\end{array} \tag{8}$$

If we solve for each of the unknowns in turn, we have

[6] Boole, loc. cit.[2] p. 16.

$$f(r)V_{1,n}=0,\quad f(r)V_{3,n}=0,\quad f(r)V_{5,n}=0,\quad f(r)V_{7,n}=0,\quad f(r)V_{9,n}=0, \tag{9}$$

where $f(r)$ is given by

$$f(r)=\begin{vmatrix} (ar-a') & (er-e') & (dr-d') & (cr-c') & (br-b') \\ (br-b') & (ar-a') & (er-e') & (dr-d') & (cr-c') \\ (cr-c') & (br-b') & (ar-a') & (er-e') & (dr-d') \\ (dr-d') & (cr-c') & (br-b') & (ar-a') & (er-e') \\ (er-e') & (dr-d') & (cr-c') & (br-b') & (ar-a') \end{vmatrix}$$

Since $f(r)$ is the same for all of the potentials, it follows that the roots which enter into Eq. (3) for this system are the same; and this is found to be true for every purely influence system. The arbitrary constants, however, are different for each potential.

Attention may be directed to the form of this determinant, namely that it is a cyclic determinant or circulant. For the five inductor alternator it is of the fifth order; for an m inductor alternator it would be a cyclic determinant of the mth order.

Fig. 1. A five inductor electrostatic alternator.

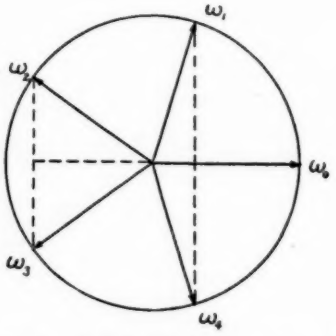

Fig. 2. The five fifth roots of unity, which play an important part in the theory of the alternator of Fig. 1.

Now a cyclic determinant of order m has the important property that it can be broken up into m factors which are rational functions of the elements of the determinant and the m mth roots of unity.[7] Each of these factors is linear in r, and by equating each separately to zero, we obtain the m roots desired.

The close connection between the geometry of these machines and the geometry of the roots of unity is extremely interesting. (Compare Figs. 1 and 2, which illustrate the case for $m=5$.)

[7] Pascal (Leitzmann), Die Determinanten, p. 73.

2. The Wimshurst Alternator[8]

This machine (Fig. 3) gives rise to a determinant of the form

$$f(r) = \begin{vmatrix} M_1 & M_2 \\ M_3 & M_4 \end{vmatrix}$$

where each of the matrices M_i is a cyclic matrix of the fourth order. By subtracting the third row (in each matrix) from the first, and the fourth row from the second, and then adding the third column to the first, and the fourth to the second, the determinant splits up into the product of two other determinants of the form

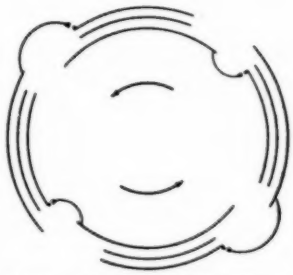

Fig. 3. The Wimshurst alternator of 1891.

$$\begin{vmatrix} a & b & c & d \\ b & a & d & c \\ e & f & g & h \\ f & e & h & g \end{vmatrix} \begin{vmatrix} a & -b & c & -d \\ b & a & d & c \\ e & -f & g & -h \\ f & e & h & g \end{vmatrix}$$

and these in turn can be broken up into four factors, namely:

$$\begin{vmatrix} b+a & d+c \\ f+e & h+g \end{vmatrix} \begin{vmatrix} b-a & d-c \\ f-e & h-g \end{vmatrix} \begin{vmatrix} a+bi & c+di \\ e+fi & g+hi \end{vmatrix} \begin{vmatrix} a-bi & c-di \\ e-fi & g-hi \end{vmatrix}$$

Each of these factors is quadratic in r, and by equating each of the four separately to zero and solving for r, we obtain the eight roots required.

Unfortunately, if the number of inductors exceeds four, this process fails. This suggests that in a certain sense the Wimshurst alternator is not perfectly symmetrical, and, in fact, if we add 4 additional inductors placed as in Fig. 4, we convert the Wimshurst alternator into a new one which is perfectly symmetrical and again leads to a cyclic determinant. Moreover, we can immediately extend the theory to machines of this type with more than four inductors.

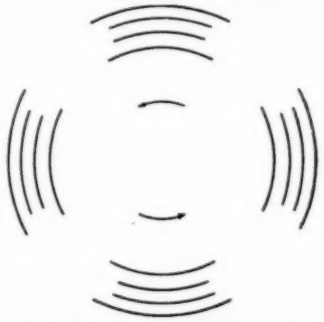

Fig. 4. A perfectly symmetrical electrostatic alternator. Any carrier (smaller arcs) is connected to the inductor (larger arcs) next following in the direction of rotation and situated on the opposite side. The inductors are fixed, the carriers rotate.

Let us now turn to a consideration of the roots themselves. At the outset we may divide these (both real and imaginary) into three classes according as their ab-

[8] J. Wimshurst, Phil. Mag. **31**, 507 (1891).

solute value is (1) less than unity, (2) equal to unity, or (3) greater than unity. In the first case the corresponding terms are transient terms, which vanish for large values of n; in the second, the corresponding terms are constants; and in the third they are permanent terms, which approach infinity as n approaches infinity.

Since the k's are functions only of the electric coefficients, the roots also will be functions only of the electric coefficients; and further it turns out that they are always ratios, or pure numbers.

In many cases it is possible to determine, from the known properties of electric coefficients, what range of values in general the roots may take, irrespective of what the particular values of the coefficients may be. For example in the case of a symmetrical Kelvin replenisher[9] of two carriers, it is possible to show that one of the roots is always less in absolute value than unity, irrespective of what the relative dimensions of inductors and carriers, angle at which the polarizing rod is set, etc.

In the case of the electrostatic alternators which lead to cyclic determinants, we obtain the roots in the form:

$$r=(A_1+B_1i)/(A_2+B_2i)$$

whence

$$\rho=\sqrt{(A_1^2+B_1^2)/(A_2^2+B_2^2)}$$

and

$$\tan\theta=(A_2B_1-A_1B_2)/(A_1A_2+B_1B_2)$$

If we put $B_1/A_1=\tan\theta_1$ and $B_2/A_2=\tan\theta_2$ we have further

$$\tan\theta=\tan(\theta_1-\theta_2).$$

The latter formula is a very convenient one for the calculation of the period of the alternator; in many cases it is found that $\theta_2=0$ whence

$$\tan\theta=\tan\theta_1.$$

The range of values which θ and ρ may take can also be established in many cases, and it is important to note that θ and ρ are functions of the electric coefficients of the elements of the machine, so that the period of reversal, which is determined by the magnitude of θ, can be varied by varying the relative capacities (electric coefficients) of the elements of the machine. The values of the ρ's will determine whether or not the machine is self-exciting; if one of the ρ's is greater than unity, the machine is self-exciting, and the greater the values of the ρ's the more rapidly the machine builds up.

We have now indicated in a general way how the quantitative theory of electrostatic systems may be developed, and have briefly indicated the

[9] A. W. Simon, loc. cit [1]

properties of these systems. We have noted that these systems are of three general types, (1) alternating systems, as exemplified by electrostatic alternators; (2) generating systems, as exemplified by machines of the Toepler-Holtz or Voss type; and (3) constant potential systems, as exemplified by electrostatic voltage multipliers.

As our final point we shall draw attention to a simple electrostatic system which can be converted at will to any one of these three types by merely changing the connections. The system, which consists of four

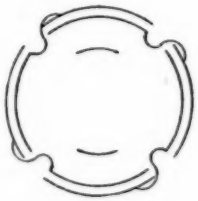

Fig. 5. An electrostatic system connected as an alternator.

Fig. 6. The system of Fig. 5 connected as a generator.

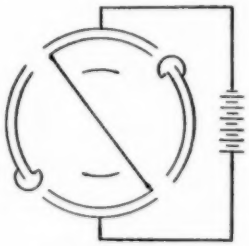

Fig. 7. The system of Fig. 5 connected as an electrostatic voltage multiplier.

fixed inductors and four revolving carriers, when connected as in Fig. 5 is an alternator; when connected as in Fig. 6 an ordinary static machine of the Voss type; and finally when connected as in Fig. 7, a constant potential machine.

In conclusion I wish to thank Prof. A. H. Compton for the encouragement he has given me in this work, as well as Mr. R. W. Barnard of the Mathematics Department for many helpful suggestions he has made regarding the mathematical treatment of the problem.

RYERSON LABORATORY,
UNIVERSITY OF CHICAGO,
March 25, 1925.

POTENTIOMETER ARRANGEMENT FOR MEASURING MICROVOLTAGES AT RADIO FREQUENCIES

By Axel G. Jensen

Abstract

The arrangement described enables voltages down to about 0.1 microvolt to be measured to within about one percent. The resistance units are wound non-inductively on a toroid so as to reduce the lengths of connecting wires to a minimum. Up to frequencies of 3×10^6 cycles, the impedance of such a unit is less than one per cent higher than the pure resistance. The potentiometer is built compactly to minimize capacity effects and for convenient use in the field.

IN the February number of the Review there appears an article by A. W. Hull and W. H. Williams[1] in which the authors describe a method for measuring microvoltages at radio frequencies. It is stated in this article that voltages of the order of 5-150 microvolts have never been accurately measured before at these frequencies and also that the use of a resistance potentiometer is out of the question for these small voltages on account of the inductive drop in the wire.

It may be of interest to your readers to know then, that the American Telephone and Telegraph Company and the Bell Telephone Laboratories, Incorporated, have for some time past been measureing voltages of this order of magnitude in connection with their measurements of field strengths from broadcasting stations, and furthermore, in measuring these voltages, are using a resistance potentiometer arrangement, which allows measurements of voltages down to about 1/5 of a microvolt with an accuracy of about one percent.

In the accompanying figure there is shown a schematic diagram of the potentiometer arrangement in connection with a receiving set for radio signals.

The current I from the vacuum tube generator flows through a 700-ohm thermocouple in connection with a Weston micro-ammeter, and from the thermocouple passes through the potentiometer P.

The resistance units in this potentiometer are wound non-inductively (reverse loop winding) on a hard-rubber toroid so that the points a and e are close together and the points e and c directly opposite on the toroid, thereby reducing the length of the connecting wires abe and cde to a minimum.

[1] Hull and Williams, Phys. Rev. **25**, 147 (February 1925).

The capacity of such a non-inductive winding is small and the inductance may be calculated by the following formula[2]

$$L=2l(\log_e d/\rho+1/4-A)$$

in which l is the total length of wire, ρ the radius of wire, d the distance between adjacent turns, and A a constant varying from 0 to .45 as the number of turns varies from 0 to infinity. The value of A is .25 for a coil of four turns, and it will therefore be safe to disregard the two last terms in the formula, since all the coils in the potentiometer have more than four turns. Applying this formula to the coarsest wire used in the potentiometer, namely No. 36 B. & S. manganin wire D.S.C., we get $d/\rho=3.5$ and thus $L=2.45$ cm per unit length, while the resistance of the wire is 30 ohms per unit length.

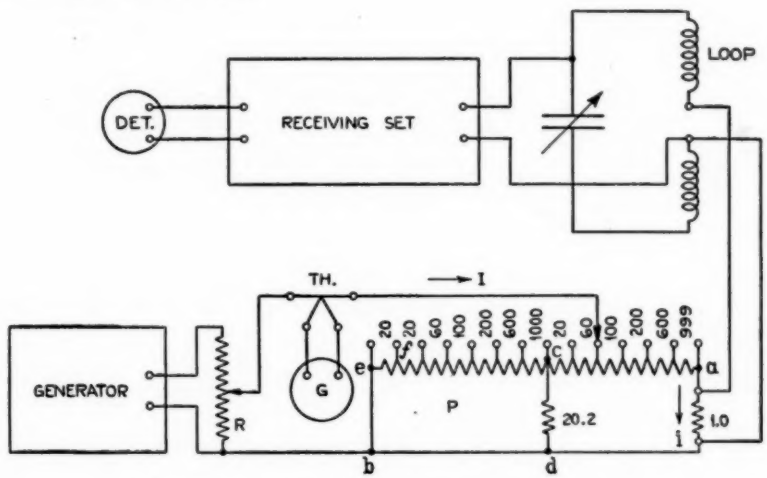

Fig. 1. Diagram of potentiometer arrangement.

This gives at 750,000 cycles an inductive drop which is 3.5 percent of the resistance drop and thus an impedance which is equal to $\sqrt{1^2+.035^2}$ or 1.0006 times the pure resistance of the wire. It will be seen that not until the frequency is increased to about 3,000,000 cycles will the impedance be as much as one percent higher than the pure resistance.

For the finer wire the relative excess of inductive drop over resistance drop will be still smaller, so that the entire potentiometer will attenuate the current with an accuracy of one percent or better up to frequencies of about 3,000,000 cycles.

The one ohm unit in the output side of the potentiometer is made up of a piece of No. 36 manganin wire approximately 3.5 cm in length and

[2] See E. B. Rosa, Bull. Bur. Stand. **4**, 301 (1907-8).

arranged bifilar so that we may use the same formula as before in calculating the inductance. We have here $A=0$ and d/ρ approximately 5, so that $L=13$ cm and $\omega L=.06$ ohm at 750,000 cycles. The impedance is thus approximately 1.002 ohm or only 1/5 percent higher than the pure resistance.

The highest current attenuation is obtained with the movable arm of the potentiometer at f, in which case the output current i is 10,000 times smaller than the input current I, and since the thermocouple combination used will measure one milli-ampere conveniently it is possible to determine voltages down to about 1/10 microvolt with an accuracy of one percent or better.

By means of the potentiometer shown in the figure the following ratios of i/I can be obtained: .0001; .0002; .0005; .001; .002; .005; .01; .02; .05; .1; .2; .5 and 1.0. These ratios were checked step by step at 750,000 cycles by means of a calibrated detector meter in the output of the highly sensitive receiving set connected up to the potentiometer, and in no case was the discrepancy between the calculated value and the measured value found to be more than one percent.

The potentiometer is built very compactly in order to minimize capacity effects; in fact, the entire potentiometer including the switch is enclosed in a copper can 3 inches in diameter and 3 inches high. The potentiometer, thermocouple, meter, and current adjusting rheostats are all contained in a copper box $10\times7\times7$ inches, and the generator is enclosed in a similar box so that the complete measuring equipment may be used conveniently in the field in connection with a portable receiving set.

In cases where portability is not essential it should be possible to measure still smaller voltages by using a sensitive galvanometer in connection with the thermocouple. Also it should be possible to increase the sensitivity of the arrangement still further by replacing the one ohm output resistance by a small known inductance, for instance of the type described by Hull and Williams.

BELL TELEPHONE LABORATORIES, INCORPORATED,
RESEARCH DEPARTMENT,
NEW YORK, N. Y.
March 13, 1925.

VARIATION OF YOUNG'S MODULUS WITH TEMPERATURE FROM VIBRATION MEASUREMENTS

A. L. KIMBALL, JR. AND D. E. LOVELL

ABSTRACT

A tuning fork of the metal being studied was mounted in an electric furnace and one prong was connected by means of a thread to a stylus which recorded the motion of the prong on a moving plate. Thus the frequency was measured to 1/10 percent. Curves obtained for a *3.5 percent nickel steel* and for a *soft machine steel* (.15 percent C) are practically identical, the modulus decreasing 10 percent as the temperature increased from 20° to 350°C and 16.7 percent for the change from 20° to 500°C. This suggests that the temperature variations of the modulus may be a fundamental property of the atoms, unaffected by the size of the crystals.

PURPOSE AND SCOPE OF INVESTIGATION

ALTHOUGH previous work has been done in this field, the results obtained, even for a substance of the same composition, have shown wide variations with different investigators. Furthermore, owing to the tendency of a metal, such as steel, to assume a very slight plastic deformation under stress, which increases with time, the usual statical method of point by point deflections is subject to error. The length of time which is required in making the observations may have a decided effect in accurate work.

In order to overcome this difficulty, in this work the variation of Young's modulus with temperature was determined from accurate measurements of the frequencies of tuning forks, a method which appears to have been little used.[1] The amplitude of the vibrations was comparatively small, so that the maximum stress was less than one tenth of the elastic limit of the material. The frequency was about 20 cycles per second, so that each stress cycle during the vibration required about 1/20 of a second for its performance.

APPARATUS AND METHOD

The apparatus is shown in Fig. 1. The fork *F*, with prongs about 55 cm long by 2.5 cm wide by .64 cm thick, was clamped in the asbestos oven heated by an electric coil. The clip *A* was suddenly pulled off the

[1] K. R. Koch and R. Dieterle, Ann. der Phys. **68**, 441 (1922);
Mallock, Proc. Roy. Soc. A**95**, 429 (1919);
H. M. Dadourien, Phys. Rev. **13**, 337 (1919);
Iokibe and Sakai, Phil. Mag. **42**, 397 (1921).

tips of the fork, starting a vibration about one quarter of an inch in amplitude. One side of the fork was connected to a fine wire *W* which passed through a small hole in the oven and was attached to a light wooden stylus *S* with a needle point on its end. The wire was kept taut by a small spring so that the tip of the stylus followed the vibratory motion of the fork exactly. Time was recorded by another stylus which registered seconds from a seconds pendulum. The vibration and time records were traced side by side on the smoked glass plate about one meter long which was pulled along at a constant rate of about 4 cm per second by an electric motor. With this apparatus it was possible to obtain frequency measurements accurate to within less than 1/10 percent. This required that the temperature be measured to within a degree or two, in order that errors from this cause be kept within the same limit.

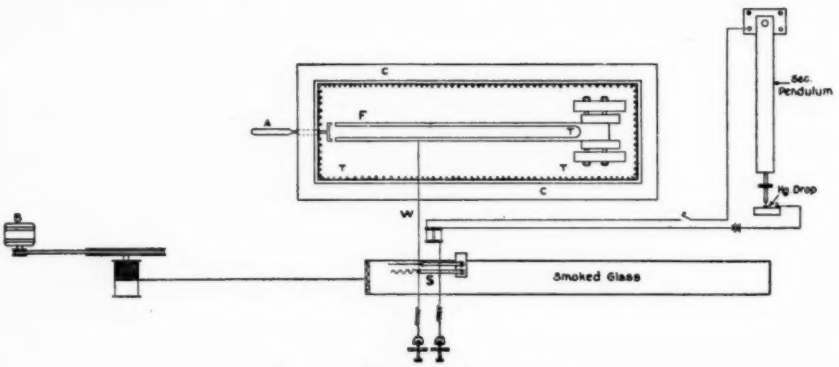

Fig. 1. Diagram of apparatus.

A uniform temperature distribution in the fork was produced by placing over it a conducting shield of sheet copper not shown in the figure. Temperatures up to 350°C were measured by mercury thermometers; and for higher temperatures a thermocouple was used. By trials and suitable calibrations, it was found that an accuracy of within one or two degrees could be obtained.

Results

Two different kinds of steel were tested in this study, 3.5 percent nickel steel and 0.15 percent commercial carbon steel.

A complete series of observations was taken upon two 3.5 percent nickel steel forks of the form shown in Fig. 1, each machined out of a single piece of heat treated steel. A series of measurements also was made upon a pair of 3.5 percent nickel steel bars clamped together in the form of a fork. All of the nickel steel was of the same chemical composition which

was as follows: C, .35 percent; Si, .21 percent; S, .020 percent; P, .018 percent; Mn, .58 percent; Ni, 3.52 percent.

The heat treatment consisted of oil quenching at 850°C and drawing at 650°C. The size of the bars from which the test pieces were cut was 100×9×4.2 cm. The plane in which vibrations took place was perpendicular to the plane of rolling of these bars.

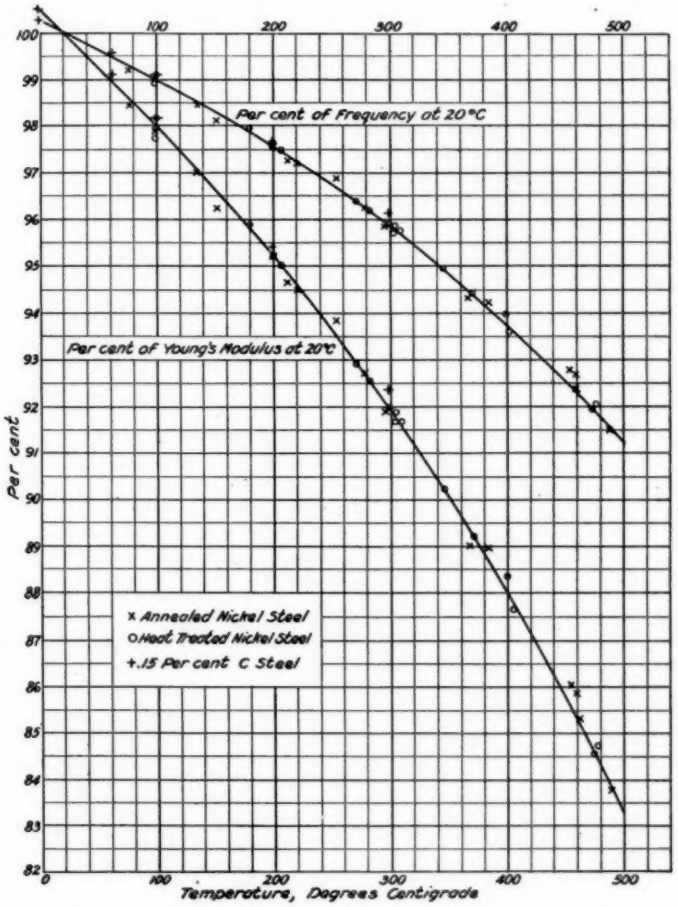

Fig. 2. Curves showing decrease of Young's modulus with temperature for 3.5 percent nickel steel and .15 percent carbon steel.

The .15 percent carbon steel was an ordinary machine steel. The tests were made on a pair of bars clamped together in the form of a fork.

The curves in Fig. 2 show the final results of the measurements. The upper one shows the decrease in vibration frequency with increase of temperature and the lower one the corresponding decrease in Young's modulus, in each case measured in percent of the value for 20°C. The

curve for Young's modulus was obtained directly from the frequency curve by using the relation

$$f = K\sqrt{E/\rho}$$

where f = frequency
E = Young's modulus
ρ = density
K = proportionality factor depending upon the shape of the vibrating body and its mode of vibration.

A small correction was necessary because the linear dimensions of the vibrating fork increase with temperature and the density ρ decreases.[2] Every point on the curves represents the average of from one to five records in each of which the frequency was determined from the average of from four to eight measurements.

A word should be said about the effect of various damping forces upon the frequency. It is well known that the period of a natural vibration is decreased slightly under the influence of damping. This effect was looked for in these experiments but was found to be within the limits of error. When a suitable friction was applied so as to increase the decrement four or five times, no change in frequency could be detected. Since the applied frictional force was much greater than that of the air, it was concluded that the effect of air friction on frequency was negligible. When the temperature was above 400°C the damping was notably greater, but even here the change in frequency, due to this cause, was within the limits of error.

The most interesting thing about the curves obtained seems to be that all points fall upon a continuous curve, or very nearly so, whether the nickel steel or the carbon steel was tested and whether the nickel steel was heat treated or annealed. This result suggests that the temperature variation of Young's modulus for these metals is little affected by variation of the size and arrangement of the crystals, but is a more fundamental property which is related to the atoms themselves.

These results are interesting in view of the fact that "elinvar," an alloy which shows practically no variation of Young's modulus with temperature, is also a nickel iron alloy. The nickel content of elinvar, however, is over 30 percent. The various peculiarities of nickel iron alloys of this type have been the subject of special investigations.[3]

RESEARCH LABORATORY,
GENERAL ELECTRIC COMPANY,
SCHENECTADY,
December 31, 1924.

[2] Barton, Text Book of Sound, p. 298.
[3] G. E. Guillaume, Proc. Phys. Soc. London, **32**, 374-404 (1920).

AN APPROXIMATE DETERMINATION OF THE DEPTH OF COMPRESSION IN COPPER BARS DURING IMPACT

By E. W. Tschudi

Abstract

Duration of impact of copper bars and of copper plated steel bars.—As in previous experiments, the duration of impact was measured by means of a Duddell-type oscillograph connected in series with the pair of colliding bars, each of which was suspended by four wires adjusted so that the plane ends struck squarely. In all cases the mass of each bar tested was the same, 2400 gm. By trying three diameters of contact area d, it was found that the time varies as $1/d^{1/2}$; it also varies as $1/v^{1/5}$; hence $t=A/d^{1/2}v^{1/5}$, where A has the values 9.7×10^{-4} and 12.35×10^{-4} c.g.s. units for these steel and copper bars. The steel bars were then plated with coherent copper deposited electrolytically to thicknesses of .017, .038, .064 mm. The time for the two thick films came out the same as for solid copper, while that for the thinnest film was between that for copper and that for steel. These results indicate that the thickness of the surface layer whose elastic constants determine the time of impact is only about .03 mm. In the case of spherical ends of 1.27 cm radius, impact at a velocity as low as 10 cm/sec. resulted in flattening the ends, the pressure exceeding the elastic limit for steel.

Introduction

TWO distinct experiments have been previously reported which led to the conclusion that the separation of two bars, with plane ends, after an end-on collision was due to a local compression in the immediate vicinity of the common surface of contact and not to a compressional wave which traversed the length of each bar, was reflected and returned to the contact ends. The first[1] of these was performed with a slow speed model of colliding bars which consisted of two helical springs with each coil weighted and the colliding ends fitted with brass annular rings. It was found that the springs separated when the compressional wave had traversed but one fourth the length of each spring.

In the second experiment[2] a steel bar was made to strike against another cylindrical piece of steel whose mass equalled the mass of the bar but whose length was only one sixth that of the bar. The duration-velocity curve for this combination was identical with the curve for two similar bars. In general, the nature of all duration-velocity curves indicated that the duration of impact bore a definite relation to the initial velocity of impact and was not a constant for all velocities as predicted by the com-

[1] Tschudi, Phys. Rev. **18**, 423 (December 1921).
[2] Tschudi, Phys. Rev. **23**, 756 (June 1924).

pressional wave theory. Wagstaff[3] aimed to show, by the use of bars with rounded ends, that both the compressional wave and local compression enter into the problem, the former predominating in the case of very long bars and the latter alone controlling the process in the case of short bars, i.e., that the shorter the bars the more nearly does Hertz's theory[4] of local compression for colliding spheres hold. The author has found, as will be shown in this paper, that the use of bars with rounded ends proved unsatisfactory because of stresses which exceeded the elastic limit; and further, that for plane ends the duration of impact varies with the area of contact at any given velocity.

These previous experiments suggested the problem of determining the order of the depth of compression. This was the purpose of the present experiments which were performed with copper bars and with steel bars of the same mass with their colliding ends copper plated.

The Apparatus

The bars were each suspended in much the same manner as in the earlier work,[2] from knife edge supports by two bifilar suspensions. The upper end of each strand of these suspensions terminated at an adjusting screw which permitted a four fold adjustment for each bar. An electromagnetic release held one of the bars, drawn aside, in the proper position from which it could be released at will. The length of time in which an electric current flowed through the bars during a collision determined the duration of the impact. It was found that additional wires, used for current carriers, hindered the motion of the bars and altered the value for the duration of impact. Hence the suspending strands themselves were used to carry the current. The relative initial velocity of impact was calculated from the height through which the deflected bar dropped. (The second bar was kept at rest initially.) This height was determined with a cathatometer which measured accurately to thousands of a centimeter.

In the present experiments an oscillograph was employed for measuring the duration of impact. A special camera which required a five-foot length of film was employed. The peripheral speed of the camera drum was approximately 10 meters per second. No effort was made to damp the element critically, as was done in the earlier experiments because the contact resistance was of no concern here. Since the camera shutter was open for only one revolution of the drum, close coordination was required between the release of the deflected bar and the opening of the shutter.

[3] Wagstaff, Proc. Roy. Soc. **A105**, 544 (1924); also Phil. Mag. **48**, 147 (1924).
[4] Hertz, Miscellaneous Papers, p. 146, 1896.

This was accomplished by the use of a single-pole double-throw switch which in the maximum displacement of the pole was about 2 cm in the vertical. With the pole in the neutral position, the one bar drawn aside, and the camera drum rotating, a catch was pushed aside which allowed the pole to fly upward under the influence of a spring. The circuit containing the electromagnet was thereby closed and the bar released. An instant before the two bars came in contact, the pole was pushed down through the neutral position and the circuit which actuated the camera shutter was closed.

The circuit containing the two bars and oscillograph element contained no inductance, but a resistance of four lamps in parallel was required to protect the element. A two volt cell supplied the requisite current.

The Experiments

Before any records could be obtained, it was of the utmost importance to adjust the bars carefully. Not only was it necessary that the two bars be horizontal but, far more important, that their colliding ends be parallel. These conditions were obtained by the use of the eight adjusting screws. Adjustments were completed only when no light could be seen through the junction of the colliding ends, with both bars in their equilibrium positions, when observed in two directions perpendicular to each other. The stand of the electromagnetic release was first stationed so as to permit the bar which was to be deflected, to be raised to the desired height and then shifted laterally until its stop and the opposite ends of the bars fell in the same line. This latter adjustment, if properly made, assured a collision in which the colliding ends hit true. When this was not accomplished the oscillogram registered this fact, and a small shift of the stand corrected the fault.

Two satisfactory exposures were obtained for each velocity of impact before proceeding with another velocity. A duration-velocity curve was obtained for a pair of copper bars of length 54.2 cm, diameter 2.54 cm, and mass 2430 gm. A similar curve was obtained for a pair of steel bars of the same diameter and practically the same mass, but of length 61.3 cm. These curves are both given in Fig. 1.

The steel bars were then fitted with copper plugs so that the bars appeared to have a thickness of 0.32 cm of copper on the colliding end of each. The purpose of these plugs was to determine if that thickness was sufficient to yield the same results as those of copper bars. Unfortunately, it was difficult to screw these plugs into the steel bars sufficiently tightly without marring the faces of the plugs. Nevertheless, a series of tests was

made which resulted in a smooth curve that lay far above the copper curve at very small velocities but came close to it at larger velocities.

Since copper cannot be deposited upon steel from a cupric solution it was necessary to deposit a copper base from a cuprous solution. The following recipe was used in preparing the cuprous solution: water, 3.75 liters; sodium cyanide, 64.0 gm; copper cyanide 56.8 gm; ammonium chloride 9.5 gm. Before employing this solution, the customary care was taken to clean thoroughly the ends of the steel bars that were to be plated. The cleaning process consisted in rubbing the surfaces with fine emery paper then dipping them into a boiling solution of concentrated potassium hydroxide, rubbing with scouring powder, dipping again in the alkaline solution and finally rinsing in tap water.

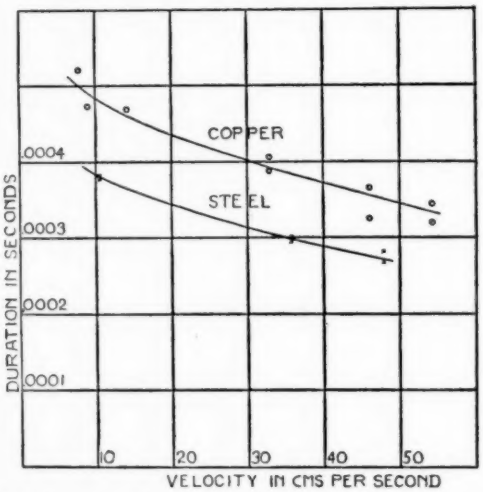

Fig. 1. Duration of impact as a function of velocity of impact, for steel and copper bars.

In the electrolytic bath, the copper anode was flat on the bottom of the vessel. The bar was thrust into the solution sufficiently to wet only the surface to be plated and was clamped in a vertical position. The surface tension of the liquid caused it to climb up the side of the bar about 0.32 cm A current of 0.1 ampere was sent through the cell for thirty minutes. This length of time was found to be a minimum in order to deposit a sufficient amount of copper to form a base for the deposition from a cupric solution. It was impossible to use the cuprous solution to deposit the requisite thickness of copper because this deposition was found to be of a spongy nature when continued over a period of several hours. The deposition from the cupric solution upon the base from the cuprous solution was, however, of the same smooth, lustrous character as when deposited upon a pure piece of copper.

After removal from the cuprous cell, the plated portion of the bar was cleaned as before with the exception of the rubbing with emery paper. In the cupric cell, a current of .05 ampere was maintained. A copper sulphate solution was used in this cell.

The duration-velocity curve for the bars with the first deposition from the cupric solution is given in Fig. 2, where also the curve for the copper bars is repeated. We have here a comparison of pure copper bars with steel bars with copper plated ends, each having the same mass and diameter, so that the impact relations are practically the same.

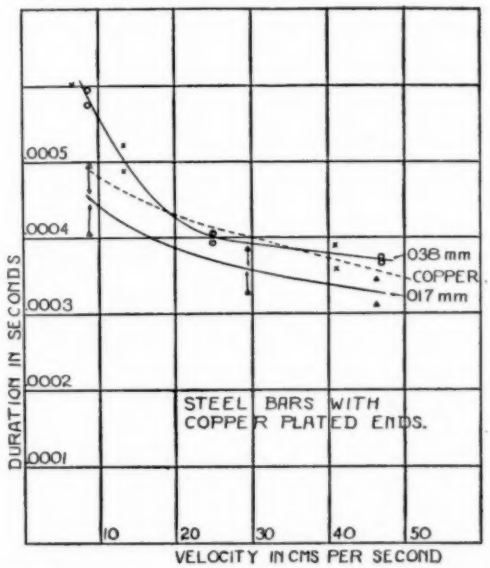

Fig. 2. Effect of plating steel bars with copper, on the duration of impact.

An additional layer of copper was then deposited from the cupric solution, with the purpose of determining whether a thicker layer would produce a duration-velocity curve which lay above the one for the first layer. This, however, was not found to be the case. The points corresponding to the thicker layer are indicated by small crosses in Fig. 2. The closeness of these points to the first curve indicates that the first thickness of copper was sufficient to produce results similar to those of pure copper bars.

The copper deposition was next removed from the steel bars in a lathe. It is worthy to note that the plated copper was found to be firmly fastened to the steel and did not peel off under the tool.

Again the ends of the steel bars were plated from the cuprous solution, but no additional copper was deposited from the cupric solution. Another

series of tests were made. The resultant duration-velocity curve, given in Fig. 2, fell below the curve for pure copper bars but above the curve for steel bars with unplated ends.

In calculating the thickness of copper deposited it was assumed that the form of the deposition was in the shape of a cup 0.32 cm deep with walls and bottom of the same thickness. The first deposit of copper was then computed to have a thickness of .038 mm, the second .064 mm, and the third .017 mm. One can conclude then that the equivalent thickness of deposited copper on steel bars which will give the same impact results as pure copper bars of the same mass and diameter lies between .02 mm and .04 mm.

Effect of Change of Contact Area

The question arose whether or not the duration of impact varied, at any given velocity, for different contact areas. In order to answer this question, the colliding ends of the steel bars were turned down to 1.90 cm for a distance of 0.32 cm back from the end. A duration-velocity curve was then obtained which is given in Fig. 3. The same ends were then turned down to 1.27 cm diameter and another curve obtained which is likewise given in Fig. 3. The curve for the steel bars with diameter 2.54 cm is repeated here. It will be noticed that with a decrease in the common area of contact the duration of impact increases. Evidently the duration of impact of a pair of bars means nothing unless the common area of contact is specified.

The relation

$$t = c_1/d^{1/2} \tag{1}$$

where t is the duration of impact and d the diameter of the circular contact area, agrees with experimental curves very well. In the following tables it will be seen that, for any definite velocity, c_1 is nearly constant.

$v=10$		$v=20$		$v=30$	
d	$c_1\times10^4$	d	$c_1\times10^4$	d	$c_1\times10^4$
2.54 cm	6.12	2.54 cm	4.57	2.54 cm	4.94
1.90	5.85	1.90	4.80	1.90	4.96
1.27	6.19	1.27	5.32	1.27	5.02

Likewise, for any given contact area, the relation

$$t = c_2/v^{1/5} \tag{2}$$

holds admirably for all cases. This form of the velocity function has been agreed upon by all investigators, whether they used spheres, bars with rounded ends, or bars with plane ends. Combining (1) and (2) we have

$$t = A/d^{1/2}v^{1/5} \tag{3}$$

The coefficient A is not a universal constant, but varies with the substance. Its values for steel and copper are 9.7×10^{-4} and 12.35×10^{-4} respectively, in c.g.s. units.

The steel bars were next rounded so as to have a hemispherical surface of 1.27 cm radius. Upon allowing the bars to collide, it was noticed that the clear metallic ring which had accompanied all previous collisions with plane ends, was lacking, and instead that a dull thud sounded as though two bars of lead had collided. Examination of the rounded ends showed a small flat area of about 1/2 mm diameter, indicating that the elastic limit had been exceeded and the ends of the bars had been mashed in. This occurred at the smallest velocity at which measurements were made. Successive blows at the same velocity increased the area of the

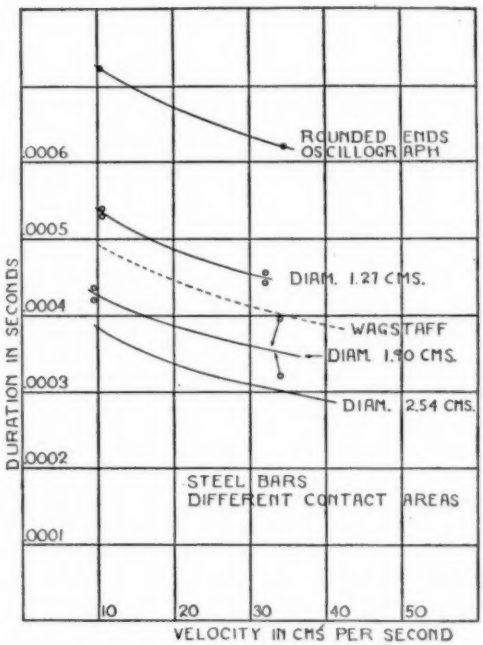

Fig. 3. Effect of contact area on duration of impact.

flattened portion. Examination of the oscillograms showed that there was no definite point at which the current had broken and therefore no measurement of the duration of impact could be made. A condenser method for measuring the duration of impact would not have disclosed the fact that the impact had been erratic, which emphasizes the necessity of an oscillograph for making measurements of this kind.

The bars were again rounded so as to expose unstrained surfaces and allowed to collide at the same velocity as before. Three successive

collisions were recorded. The resultant oscillograms proved satisfactory this time. The duration of impact, as measured from them, was found to grow smaller as the number of impacts increased, due, no doubt, to the increase in contact area. Similar results were obtained at a greater velocity. They are tabulated below.

$v=10.28$		$v=34.80$	
Trial	Duration	Trial	Duration
1	7.23×10^{-4}sec.	1	6.20×10^{-4}sec.
2	6.82	2	5.32
3	5.75	3	4.35

The durations of impact for the first trial at each of the two velocities are plotted in Fig. 3. In the same figure is plotted a broken curve for steel bars, of practically the same dimensions, from values given by Wagstaff,[3] who used a condenser discharge method for measuring the duration of impacts.

In the classical relation between the impulse and change in momentum of colliding bodies, if it be assumed that the force during the impact varies as $F=B \sin(\pi t/t_1)$ where t_1 is the duration of the impact, then it can readily be shown that the maximum force exerted during impact is $B=(mv-mu)\pi/2t_1$. Substituting values from the preceding table, for example, $t_1=7.23\times10^{-4}$, $v=10.28$, we have $B=5.22\times10^7$ dynes. This force is distributed over an area of 1.96×10^{-3} cm.^{2} Hence the force per unit area is computed to be 2.66×10^{10} dynes, more than twice the maximum limit of elasticity tabulated for steel.

The author is greatly indebted to the Bureau of Standards for the loan of the oscillograph used in these experiments and takes this opportunity to express his thanks and obligation. Suggestions and criticisms offered by Dr. J. S. Ames during the course of the experiments were of high value and greatly appreciated.

JOHNS HOPKINS UNIVERSITY
March 18, 1925.

INTERFERING EFFECT OF TONES AND NOISE UPON SPEECH RECEPTION

By Vern O. Knudsen

Abstract

The interfering effect upon speech of tones and noise was measured by determining the percentage of vowel, consonant and word articulations correctly heard by an observer who listened in the presence of a tone or noise to meaningless monosyllables spoken at a distance of 2 meters. The interfering tones varied in pitch by octaves from C_2 (128 d.v.) to C_7 (4096 d.v.) and in loudness from slightly above minimal audibility to near the painful limit. The interfering effect increases with increasing loudness of tone or noise at an accelerated rate; for tones with a loudness less than the loudness of the speech, the effect is almost independent of the pitch, but as the interfering tone becomes louder, the tones of lower pitch produce a relatively greater and greater interference. These results are consistent with the auditory masking data of Fletcher, Wegel and Lane. A noise produces twice the interfering effect of a tone of the same loudness. These results indicate that for good hearing in an auditorium the speech energy should be from 1000 to 10,000 times the energy of any interfering noises, and that sound-absorbent materials for the reduction of noises in auditoriums should absorb equally tones of all pitches below C_7. Some experiments with rather deaf persons will be reported elsewhere.

THE work described in this paper is part of a larger program, the object of which is to determine quantitatively the influence of the various factors which affect the quality of speech in an auditorium. The specific object of the present problem, as the title suggests, is to determine (1) the relative interfering effect upon speech of tones of different pitch and loudness, and (2) the interfering effect upon speech of typical noises of different loudness.

Telephone engineers have done considerable work upon the interfering effect of noise upon speech transmitted over various types of telephone circuits. Up to the present, however, there has been very little published upon the subject. The work of the writer differs from the work done by telephone engineers in that the writer's tests are conducted in a typical small auditorium, and the observer listens directly to the voice of the speaker rather than to the speaker's voice transmitted over a telephone circuit.

The tests were all conducted in a room having a volume of 15,000 cubic feet and a period of reverberation of 1.3 seconds. The interfering tone or noise was conducted to the observer's ears by means of a pair of telephone receivers which were adjusted so that each receiver was at a fixed distance

of 2 cm from the ear to which it was attached. The speaker, or "caller," spoke with a natural, easy, conversational voice, at a distance of two meters from the observer. The energy of the speech reaching the observer was slightly less than 10^5 times the minimal audible speech energy. Preliminary comparisons of the loudness of the speech with the loudness of tones of which the energy could be accurately determined, indicated that the loudness of the speech was approximately 47 logarithmic units.[1] This loudness of speech is comparable with the loudness of speech in an average auditorium.

The measurements were made by the usual method of articulation tests commonly used in testing the transmission efficiency of a telephone circuit. The "caller" called out meaningless consonant-vowel, vowel-consonant and consonant-vowel-consonant monosyllables, and the observer recorded what he heard, or thought he heard. By comparing the observer's lists with the lists called, the number and nature of the errors can be determined. The results of such tests are expressed as the percentage vowel articulation, the percentage consonant articulation, and the percentage "word" articulation.

The total number of speech-sounds called in making these tests was 29,000. These speech-sounds or "words" were called in groups of three, at the rate of one speech-sound each .85 of a second. Tests were made with interfering tones of C_2 (128 d.v.), C_3 (256 d.v.), C_4 (512 d.v.), C_5 (1024 d.v.), C_6 (2048 d.v.), and C_7 (4096 d.v.). Tests were also made with a typical noise as the interfering source. The interfering tones and the noises were maintained at various loudness levels, ordinarily at 20, 40, 60 and either 70 or 80 log-units. After many tests had been completed it was obvious that it was superfluous to take measurements below 40 log-units. 400 speech-sounds were called for each condition tested. Half were called by the writer, and the other half by an assistant. The observer and caller changed positions four times during the tests of each interfering condition. The tests with the same interfering source also were distributed over at least four different periods of observation. This would tend to make all of the results more nearly comparable. An indication of the uniformity of the speech and hearing of the two observers is the fact that the average percentage word articulation of one observer,

[1] This unit of loudness, proposed by telephone engineers, is very convenient. The loudness of the tone, expressed in this unit, is ten times the logarithm to the base ten of the ratio of the energy of the tone to the energy of a barely audible tone of the same pitch. For example, a tone whose energy is one million times the energy of a barely audible tone of the same pitch, is 60 log-units.

for the entire series, differed only two percent from the average of the other observer.

Results of the tests are shown in a series of curves, Figs. 1 to 3. Fig. 1 shows the results of the tests with tones as the interfering source. The percentage articulations for vowels, consonants and words are plotted as

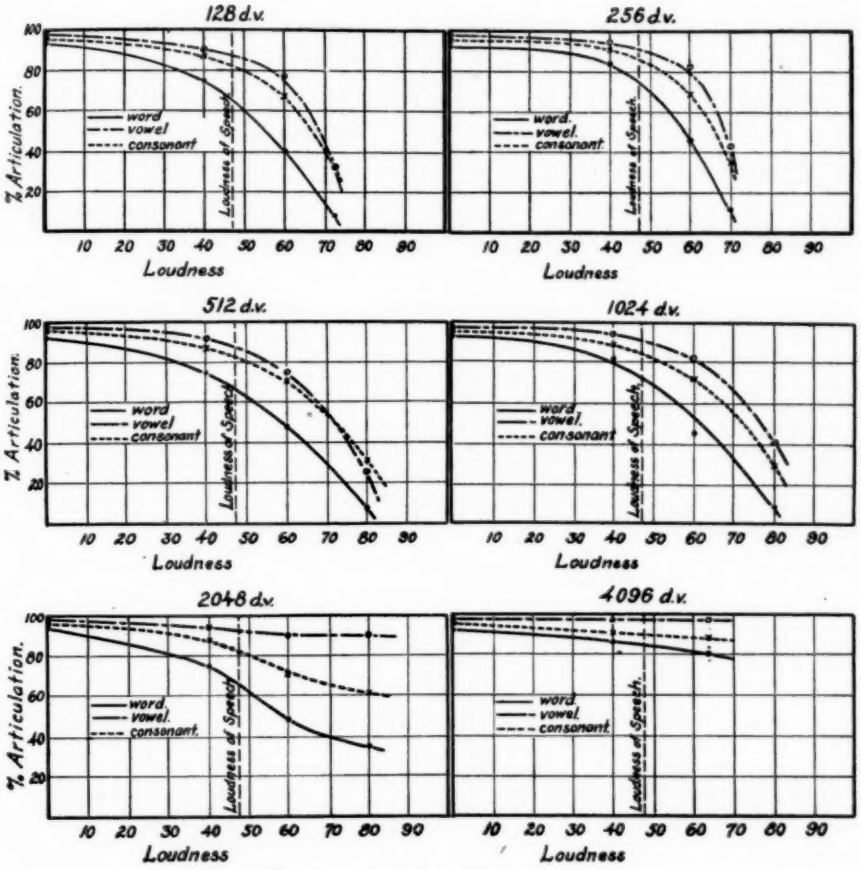

Fig. 1. Interfering effect of tones.

a function of the loudness. Fig. 2 shows the results obtained with a noise consisting of a series of clicks in the telephone receivers, produced by interrupting a current flowing through an inductance in series with the telephone receivers. Curve (1) expresses the word articulation when the frequency of the clicks was 14 per second; curve (2) the word articulation when the frequency of interruption of the clicks was 20 per second. Fig. 3 indicates how the percentage articulations for vowels, consonants and words varied with the pitch of the interfering tone, at two different loud-

ness levels, viz., 47 log-units, the loudness of the speech, and 70 log-units.

The conclusions which may be drawn from the data are as follows.

1. The interfering effect of tones of which the loudness is less than the loudness of the speech, is almost independent of the pitch of the tones. However, for very high tones, above C_6 (2048 d.v.) the interfering effect seems to decrease as the pitch rises, so that tones above C_7 (4096

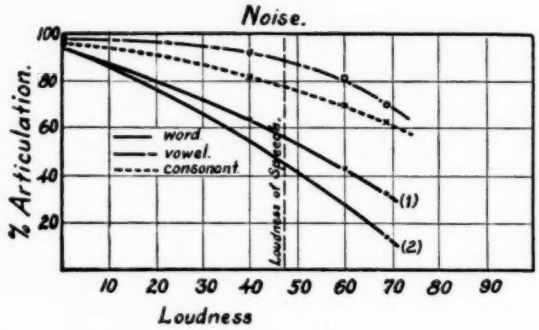

Fig. 2. Interfering effect of noise.

d.v.) should have practically no interfering effect. A tone of any pitch below C_6, equal in loudness to the speech loudness, reduces the word articulation to about seventy percent. This may be seen from an inspection of Fig. 3.

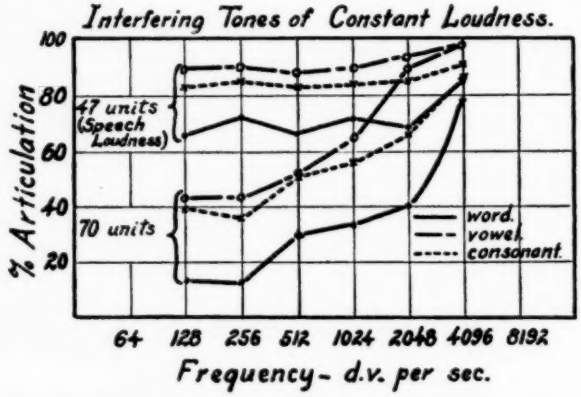

Fig. 3. Variation of interfering effect with frequency.

2. The interfering effect of tones whose loudness is greater than the loudness of the speech depends very much upon the pitch of the tones, decreasing markedly as the frequency increases. For example, at 70 log-units, the vowel, consonant and word articulations for C_3 (256 d.v.) are 43 percent, 36 percent and 13 percent, and for C_7 (4096 d.v.) are 98

percent, 85 percent and 78 percent, respectively. This conclusion is consistent with the data of Fletcher, Wegel and Lane on the auditory masking of one tone upon another. As the interfering tones become louder, the non-linear response of the ear's mechanism introduces many combinational or "subjective" tones, all of which are higher in pitch than the fundamental. Hence, as tones of low pitch become louder, they introduce many combinational tones which will lie within the important speech range. On the other hand, the tones of high pitch will introduce combinational tones of which most will be above the important speech range; therefore, when the loudness of these tones is increased, the interfering effect does not increase nearly as rapidly as it does with an increasing loudness of low tones. These results are clearly indicated in Fig. 3. It is to be noted therefore that the interfering effect of the low frequency components of noises, provided the noises are loud, is greater than the interfering effect of the high frequency components.

3. The interfering effect of tones and noises, generally, is felt more in relation to consonants than to the vowels. However, low pitched interfering tones reduce the consonant articulation only slightly more than they do the vowel articulation, whereas high pitched tones reduce the consonant articulation very much more than they do the vowel articulation.

4. A noise produces a greater interfering effect than a tone of any pitch. Thus a typical noise, of loudness equal to the loudness of the speech, reduces the word articulation to about fifty percent, whereas any tone below C_6 (2048 d.v.) of the same loudness, reduces the word articulation to only about seventy percent.

5. From an inspection of Fig. 2 it will be seen that even a little noise reduces the word articulation appreciably. Roughly, it may be concluded that the speech must be at least 30 or 40 log-units louder than the noise if the noise is not to produce a harmful effect. Expressed in energy, the energy of the speech should be from 1000 to 10,000 times the energy of the interfering noises. This indicates the necessity for extreme reduction of noises in any auditorium.

6. A practical conclusion indicated by these data is that sound-absorbent materials for the reduction of noises in architectural interiors should absorb equally, tones of all pitch below C_7 (4096 d.v.). This, of course, is also desirable from the standpoint of having no distortion of speech or music.

Similar experiments, conducted with certain rather deaf individuals who claim they hear better in the presence of a noise, indicate that they

actually hear not as well in the presence of a noise.[2] These experiments, together with other experiments and explanations pertaining to this problem, will be presented in a future paper.

The writer wishes to acknowledge the assistance of Mr. W. A. Munson and Mr. F. L. Poole. He also wishes to express his thanks for the use of articulation lists which were furnished through the courtesy of Dr. Harvey Fletcher of the Western Electric Company.

DEPARTMENT OF PHYSICS,
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SOUTHERN BRANCH.
April 7, 1925.

[2] Kranz and Fletcher have published some plausible reasons why certain of such people have an advantage over normally hearing individuals in the presence of a noise. See F. W. Kranz, Laryngoscope, March, 1924, and H. Fletcher, Volta Review, September, 1924.

BOOK REVIEWS

Die meteorologischen Messmethoden. WALTER GEORGII.—The fifty-eight octavo pages of this work constitute a section of the *Handbuch der biologischen Arbeitsmethoden* (Abt. II, Heft 4, Lief. 118) now appearing under the general editorship of Dr. Emil Abderhalden, with the assistance of 500 noted specialists.

Nothing is said about the measurements of the total intensity of insolation, nor its spectral distribution; nothing about sky brightness nor sky polarization; nor anything about the electrical state of the atmosphere. Some of these things, perhaps all, are to be discussed by other specialists.

Naturally, German instruments and German practice are stressed. American variations from either are given but little or no attention. In the main, however, that is not important, since in meteorology, as in other sciences, the exact manner of getting data is of no consequence so long as they are reliable.

Among the various thermometers described is one for measuring sunshine. This consists of a vacuum-jacketed black bulb thermometer in conjunction with a similarly jacketed clear bulb instrument. Of course the two individuals of this pair give different readings when exposed to sunshine, but the use, biological or otherwise, one can make of that difference is not obvious. This is one of the instruments we in America do not use. We prefer the pyrheliometer, for instance, which gives interpretable readings.

The measurements of atmospheric pressure, humidity, wind velocity and direction, precipitation, and other meteorological elements, are simply explained, and many of the instruments mentioned satisfactorily illustrated. Under evaporation, however, only one type of instrument is described, and that an unfamiliar one, at least to American meteorologists.

In short, the descriptions here given of meteorological instruments and their uses are very good, for the class of readers addressed, that is, those who use instruments merely as purchased tools for the collection of approximately accurate data. The book, or chapter rather, has its place, and fills it very well.—Urban and Schwarzenberg, Berlin and Vienna, 1924. W. J. HUMPHREYS

Zeemaneffekt und Multiplettstruktur der Spektrallinien. E. BACK and A. LANDÉ.—This is the first of a series of monographs, prepared under the editorship of Professors Born and Franck, which aim to cover the various divisions of the modern theory of the structure of matter in fuller detail than can be done in a single book. Its scope is confined strictly to the topics indicated by its title (excluding even such closely related matters as the Stark effect and the formulas for spectral series) and within this field it is authoritative, precise, and complete.

The theoretical section (prepared by Professor Landé) covers so much ground in a hundred pages that it is hard reading for the novice—harder, indeed, than the original papers from which it is condensed. The available space, however, could hardly be better used. The normal and anomalous Zeeman effects, the structure of multiplets, and the interval and intensity rules are very clearly discussed; then the more complicated relations which appear in spectra "*zweiter stufe*" such as that of neon; and finally the Paschen-Back effect, the magneton theory and the recent "relativistic" formulas for the separations of the multiple terms. Half-quantum numbers are introduced freely; the anomalous Zeeman separations formally explained by the assumption that the magnetic energy of the central part (Rumpf) of the atom, is to be counted twice; and the relativistic interpretation of the optical term-separations dismissed as incredible, in view of other evi-

dence. The need for a fundamental modification of existing theory, to account for these and other difficulties, is clearly stated.

The experimental part (written by Dr. Back) gives in much more detail an excellent account of the admirable technique developed at Tübingen for the study of the Zeeman effect. With an intermittent vacuum arc in a field of 38,000 gauss an actual resolving power of more than 250,000 has been attained in the spectra both of solid electrodes and of gases. The various types of complex Zeeman patterns and the methods by which these are analysed are fully described and illustrated by numerical examples and by a series of excellent photographic reproductions of original negatives.

A valuable bibliography of the subject, up to about the middle of 1924, and a table of the theoretical Zeeman patterns for systems from the doublets to the septets, complete the volume. The usefulness of the last table is impaired by the fact that it includes only the *sp*, *pd* and *df* combinations. When a second edition of the work (which the rapid advance of this field must soon demand) appears, it is to be hoped that the *g*, *h*, and *i* combinations which occur in the more complex spectra, will be included, and also those of types *pp'*, *dd'*, etc., and also that space may be available for a fuller discusion of the theory. The high price of the book might indeed have permitted the allotment of this space in the present edition.—Pp. xii+213. Julius Springer, Berlin, 1925. Unbound M 14.40; bound M 15.90. H. N. RUSSELL

Théorie Mathématique de l'Électricité, TH. DE DONDER.—In all of the changes that are taking place in our conceptions of the physical universe, Maxwell's system of equations for stationary media has so far held its own, and a consistent development of these equations, based upon the minimum number of special assumptions, is particularly welcome at the present time. Professor de Donder, of the University of Brussels, has written an excellent book, with this object in view.

Electricity is regarded as having a real existence in euclidean space. The electric potential is defined in the usual way for point, surface and volume distributions. Electric force is *defined* as the negative gradient of the potential. The electric resultant, on the other hand, is defined, with the aid of Coulomb's experimental law, as the mechanical force acting on a unit point charge. In the case of surface distributions, for points on the surface, and inside polarised distributions, these definitions lead to different results. The behavior of the potential, together with its first two derivatives, at bounding surfaces is much more fully treated than in most of the modern text-books. The author's treatment of polarised distributions, both throughout volumes and over surfaces, and his use of the vector potential in this connection, is worthy of particular note.

Electric currents are defined as electric charges in motion. Corresponding to volume and surface charges, there are volume and surface currents. Magnetic force is *defined* as the curl of the vector potential due to electric currents. In this way it is possible to develop the theory of magnetism without assuming the existence of real magnetic poles. For this purpose it is necessary to appeal to experiment, in the law, attributed to Laplace, according to which the mechanical force exerted upon a current element in a magnetic field, is proportional to the vector product of the current element and the magnetic force. In order to bring magnetic polarisation into the general scheme, it is shown that a closed current is equivalent in its effects to a magnetic doublet formed of two equal and opposite fictive magnetic poles. The author's treatment of electric polarisation is such that by a mere change of expression it applies equally well to the magnetic case. This analogy is aided by his notation; Roman letters are used for the electric quantities and script letters for the corresponding magnetic quantities.

The final book in this volume deals with the variable electromagnetic field and Maxwell's equations. The continuity of electric currents leads to the introduction of displacement currents and the first of the triads of Maxwell; Faraday's experimental

law of induced electromotive force leads to the second triad. Poynting's theorem is developed in all generality so as to include the energy dissipated in dielectric and magnetic hysteresis; and it is shown how the forces in an electric field may be interpreted with the aid of stresses in a medium.

Professor de Donder has in this admirable book made a valuable contribution to physical science. The appearance of the second volume, to include applications to the theory of electrons and electric waves, and, it is to be hoped, to bodies in motion, will be awaited with interest.—Pp. 198, Paris, Gauthier-Villars, 1925. E. P. ADAMS

Lehrbuch der Technischen Physik. Masse und Messen, Mechanik, Akustik, und Thermodynamik. GEORG GEHLOFF, editor.—This book is another product of the recent rapid development in Germany of technical physics, which has already resulted in the founding of the Deutschen Gessellschaft für Technische Physik and the Zeitschrift für Technische Physik. The book is ostensibly addressed to advanced students and engineers, but will be found of interest by many experimenters in pure physics because of the many descriptions of technical processes which may be adapted to experimentation. Furthermore it will be found a valuable book of reference in those subjects which it covers, because it contains in an astonishingly short space most of the essential theory and many of the essential facts. The condensation is so great, in fact, that the German advanced student or engineer must be recognized to be a different breed from that raised in this country if he can be successfully taught from this as a text book.—Pp. xiii+386, Johann Barth, Leipzig, 1924. P. W. BRIDGMAN

Transmission Circuits for Telephonic Communication. K. S. JOHNSON.—The purpose of the author has been to cover the general theory and principles which are applicable to the development and design of circuits and lines for association with such telephonic instruments as transmitters, receivers, and vacuum tubes. The detailed characteristics of these instruments are not discussed. Familiarity with elementary alternating current theory and complex-quantity notation is assumed; but a review of the latter, with condensed formulas, is given in one of the seven mathematical appendices.

While there are many admirable books dealing with power transmission, there has long been a need for a book dealing with the fundamental principles of telephonic circuits. The treatment is comprehensive and masterly, being of particular value to the specialist and to one whose training qualifies him to appreciate analysis in this particular field.—Pp. 326. Price $5.00. D. Van Nostrand Co., 1925. FREDERICK BEDELL

Der Radio-amateur. P. LERTES.—This book would be of interest in parts to all amateurs. It begins with a discussion of the elements of electric circuits and electricity, covers very briefly and generally all the principal methods of transmitting and receiving, both telegraphy and telephony. It is non-mathematical. Some curves are shown to explain what the author considers important parts of theory. Numerous circuits are given as well as many photographs of apparatus.

Too large a part of the book is taken up with elementary electricity and with obsolete transmission systems to make it of value to a technical man who wishes to turn radio amateur. As it stands, the remainder would satisfy the type of amateur that we know in the United States or the physicist who knows nothing of radio and wants some elementary book on the subject, but it is hardly suitable for one who wishes to build his own apparatus.

An appendix contains tables of time signal transmission, telegraphic and broadcasting schedules, and other items of interest to the amateur.—Pp. 214, figs. 114. Theodor Steinkopff, Dresden and Leipzig, 1924. R. A. HEISING

A Laboratory Manual of Experiments in Physics. LEONARD ROSE INGERSOLL.—This manual is the outgrowth of one used for many years in the University of Wisconsin in connection with the elementary courses. The 76 experiments described are for the most part standard but are well selected and include such experiments as the study of centrifugal force by means of motor driven rotating balls held in by springs, the determination of the mechanical equivalent of heat by letting shot fall repeatedly from one end to the other of a long wooden tube, the measurement of heat conductivity of several insulating materials, study of the vertical distribution of light and the efficiency of an incandescent lamp, and a study of the eye as an optical instrument with the aid of a model. The directions and notes are clear and yet concise, the result of considerable practical experience with many students. The book is well printed and illustrated and should be useful in any laboratory which has not its own printed manual of instructions. —Pp. 220, 56 fig., McGraw-Hill, New York, 1925. $2.00. G. S. F.

The "Chemical Age" Chemical Dictionary. This dictionary defines in an elementary way about 2000 of the more common chemical terms, and is intended to meet the needs of those who have occasion to consult any chemical abstracts or articles. It is said to be the forerunner of successive volumes on "Organic Substances," "Inorganic Substances" etc. It seems expensive for its size.—Pp. 158, Van Nostrand Co., New York. Printed in Great Britain, 1924. $4.50. G. S. F.

Discours de la Nature de l'Air etc. EDME MARIOTTE.—This is one of the collection of memoirs and works in the series "Les Maitres de la Pensee Scientifique" published by Gauthier-Villars. It includes a brief biographical notice and besides the Discours de la Nature de l'Air, letters on "La Vegetation des Plantes" and "Nouvelle Découverte Touchant la Vue."—Pp. 118. 3 fr. Gauthier-Villars, Paris. G. S. F.